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Facile synthesis and coupling of 3,9-dibromo-6-aryl-5*H*-dibenzo[*d*,*f*][1,3]diazepine derivatives

Manisha Tomar[a], Nigel T. Lucas[b], Klaus Müllen[c], Josemon Jacob[a,*]

[a] *Centre for Polymer Science and Engineering, Indian Institute of Technology Delhi, Hauz Khas, New Delhi, India*
[b] *Department of Chemistry and The MacDiarmid Institute for Advanced Materials and Nanotechnology, University of Otago, Dunedin 9054, New Zealand*
[c] *Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany*

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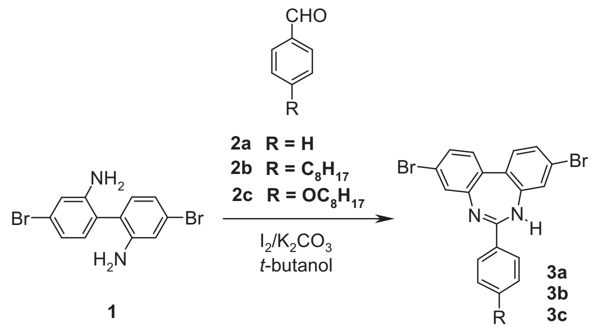
ABSTRACT

A route has been developed to prepare 3,9-dibromo-6-aryl-5*H*-dibenzo[*d*,*f*][1,3]diazepine derivatives which undergo facile Suzuki coupling to generate extended conjugated moieties bearing this unit. Single crystal X-ray studies on three of the coupled products provide valuable information on the conformation and bulk packing of these materials.

N-containing polymers have been extensively studied as active materials in various organic electronic devices. Depending on the nature of incorporation of the nitrogen atom in the monomer unit, either p- or n-type semiconducting materials are obtained. Among the classes widely investigated are oxadiazoles,[1] pyridines,[2,3]quinoxalines,[4] carbazoles,[5–7] quinolines,[8–10]benzimidazoles,[11]benzothiadiazoles,[12–15] and bis(benzothiadiazole)s,[16] and donor–acceptor type materials based on these classes have shown potential for use in organic solar cells and light emitting diodes.[17–19] Recently, we have shown that quinoline and biquinoline-based materials can be readily synthesized using a precursor route to their functionalized dibromides.[20,21] In this Letter, we describe the synthesis and characterization of 3,9-dibromo-6-aryl-5*H*-dibenzo[*d*,*f*][1,3] diazepine**3** as a new candidate for organic electronics. The phenyl derivative **3a** has been coupled with thiophene, 2,1,3-benzothiadiazole, and fluorene to generate various moieties with extended conjugation.

The synthetic approach toward the synthesis of 3,9-dibromo-6-aryl-5*H*-dibenzo[*d*,*f*][1,3]diazepine**3** is shown in Scheme 1. 2,2′-Diamino-4,4′-dibromobiphenyl **1** was converted to **3** by a simple and fast one-step reaction with an aromatic aldehyde in the presence of I_2/K_2CO_3 using *t*-butanol as the solvent.[22] This precursor approach eliminates the need for further functionalization prior to coupling and the 3,9-substitution of bromine atoms in the diazepine derivative can help to build extended conjugated molecules or its polymers and copolymers. To improve solubility, an alkyl chain was introduced into the molecule by reacting **1** with 4-octylbenzaldehyde 2**b** and 4-octyloxybenzaldehyde **2c,** to give **3b** and **3c**, respectively.

The compounds are difunctional with ideally placed bromine substituents and can serve as a precursor for the synthesis of various monomers, co-monomers, polymers, and co-polymers. 3,9-Dibromo-6-phenyl-5*H*-dibenzo[*d*,*f*][1,3]diazepine**3a** was selected as a base molecule for the synthesis and characterization of three of its coupled products. The dibromo compound **3a** was coupled with thiophene-2-boronic acid **4**, 2,1,3-benzothiadiazole-derived boronate ester **6**, and 9,9-dimethylfluorene-derived boronate ester **8**, to give a diazepine unit end-capped with thiophene **5**, 2,1,3-benzothiadiazole **7**, and 9,9-dimethylfluorene**9**, in 30%,



Scheme 1. Synthesis of 3,9-dibromo-6-aryl-5*H*-dibenzo[*d*,*f*][1,3]diazepine.

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* Corresponding author. Tel.: +91 9911061890; fax: +91 11 2659 1421.
E-mail address: jacob@polymers.iitd.ac.in (J. Jacob).

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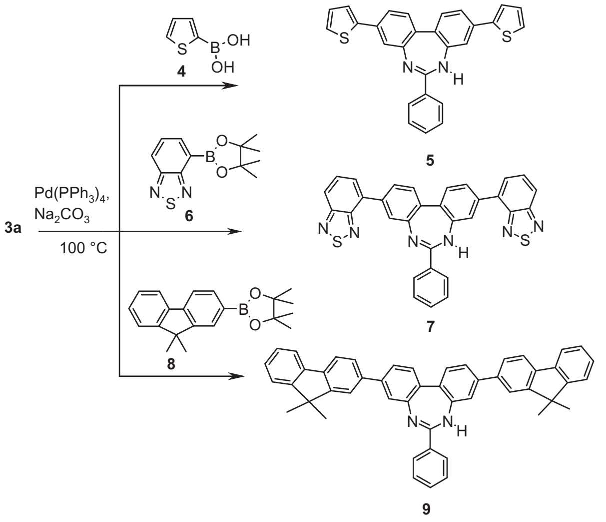

Scheme 2. Synthesis of model compounds based on 3,9-dibromo-6-aryl-5*H*-dibenzo[*d*,*f*][1,3]diazepine.

79%, and 47% yields, respectively (Scheme 2). The model compounds were characterized by ^{1}H and ^{13}C NMR, mass spectrometry, UV–vis absorption, and emission spectroscopy.

Single crystals of the dibromide **3a** (DCM/ethanol) and the model compounds **5**, **7**, and **9** (DCM/methanol) were studied by X-ray diffraction, allowing the solid-state molecular conformation and packing to be probed.[23] In all structures the phenyl-5*H*-dibenzo[*d*,*f*][1,3]diazepine unit adopts the same boat conformation with the pendant 6-phenyl ring close to parallel with the C1–C6 benzo ring (Fig. 1); the intervening imine group shows a C2–N1–C13 bond angle between 121.7° and 123.7°, suggesting a degree of conjugation between the phenyl ring and benzo ring of the monomer backbone. The twist angle between the two benzo rings spans the range 30.7° (**3a**)–40.57° (**9**), increasing as the size of the substituent increases. Monomer **5** exhibits the most planar conformation overall (the thienyl groups are rotated 18.9/3.7° with respect to the benzo groups to which they are attached).

The structures of **5**, **7**, and **9** all contain methanol molecules hydrogen bonded to the diazepine ring, linking to neighbor monomers, most notable in $\mathbf{5}\cdot(CH_3OH)_4$ where a chain of four methanol molecules bridge the diazepine N–H and N groups of adjacent molecules. When solvents other than methanol were used in monomer crystallizations, powders rather than single crystals were obtained, indicating the importance of methanol in forming H-bonded networks as part of the bulk crystalline structure. In addition to H-bonding, the structure of benzothiadiazole-substituted **7** also shows chains of close S···N contacts (3.168/3.322 Å) that run along the *a*-axis (see Electronic Supplementary data for packing diagrams). To date only five dibenzo[*d*,*f*][1,3]diazepines have been structurally characterized,[24–28] none of them 3,9-substituted. The dibenzo twist angle for these structures ranges between 30.8° and 35.5° when the rings are unsubstituted; a 1,11-dimethyl-substituted dibenzo[*d*,*f*][1,3]diazepine is forced into a more twisted conformation (57.4°) due to steric hindrance between the methyl groups.

The optical properties of the model compounds were measured in dilute THF solutions (10^{-5} mol/L) at room temperature. A plot of the extinction coefficient versus wavelength for **5, 7,** and **9** is shown in Figure 2. 3,9-Dibromo-6-aryl-5*H*-dibenzo[*d*,*f*][1,3]diazepine has its absorption maximum at 278 nm. When the diazepine moiety is end-capped at the 3,9-positions with thiophene and fluorene units, the absorbance maxima is observed at 304 and 314 nm, respectively, which is attributed to the π–π^* transition. End-capping the dibenzodiazepine molecule with 2,1,3-benzothiadiazole induces a larger red shift and the absorbance maximum shifts to 356 nm. The observed red shift in the absorption maximum on coupling of the diazepine unit with other aromatic moieties can be attributed to extended π-conjugation. Despite the more extended π-system of the fluorene group over the thiophene, the absorbance maximum for the fluorene model compound **9** is only marginally greater than the thiophene-substituted **5**. The extent of conjugation will depend on the twist angle between the diazepine core and the neighboring units; the solid-state structures above reveal larger twist angles (35.5/41.5°) for **9** compared with **5** (3.7/18.9°). If solution behavior mirrors that seen in the solid-state then the larger size of the fluorene may be partially negated by a larger twist angle and poorer π-conjugation with the dibenzodiazepine core.

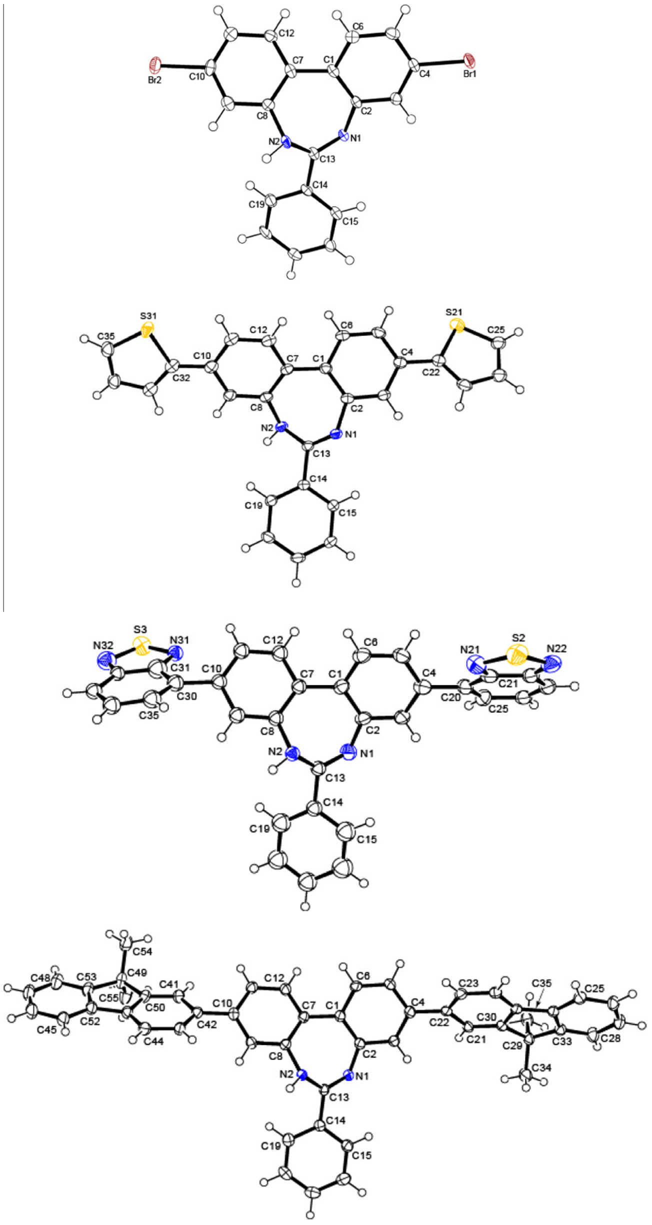

Figure 1. ORTEP representations of crystal structures of **3a**, **5**, **7**, and **9**. Methanol/dichloromethane solvate molecules have been omitted for clarity. Displacement ellipsoids are depicted at 50% probability.

The photoluminescence spectra for the coupled compounds are depicted in Figure 2. Compounds **5** and **9** emit in the blue region of the spectrum with emission maxima centered at 441 and 436 nm, respectively. Dibenzodiazepine end capped with

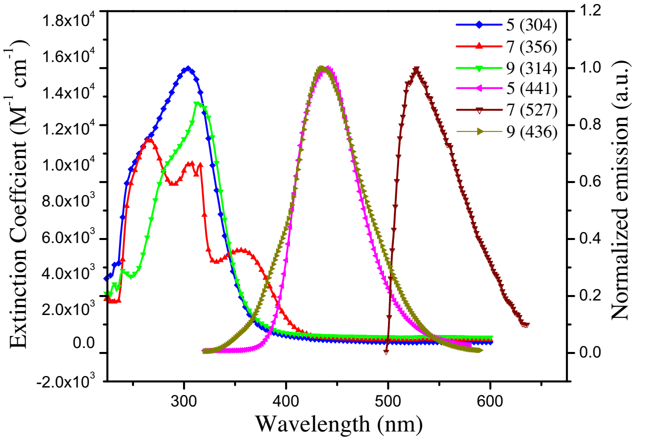

Figure 2. UV–vis absorption and emission spectra of **5**, **7**, and **9** (the observed maxima shown in brackets) in THF solution.

2,1,3-benzothiadiazole units **7**, has its emission maximum red shifted to 527 nm. The observed Stokes shifts for **5**, **7**, and **9** are 137, 171, and 122 nm, respectively. The observed large Stokes shift may be attributed to large structural reorganization between the ground and excited state, suggesting a large twist between the diazepine unit and the neighboring aromatic moieties in solution.[29,30]

In conclusion, we have developed a simple, direct, and reliable precursor route to 3,9-dibromo-6-aryl-5*H*-dibenzo[*d*,*f*][1,3]diazepine derivatives which undergo facile Suzuki coupling reaction with other aromatic moieties, a potential pathway to new π-conjugated organic materials.

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Supplementary data

Supplementary data (synthesis, NMR, MS and X-ray data) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2013.08.107.

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23. *Crystal data for* ***3a****:* $C_{19}H_{12}Br_2N_2$, M = 428.13, monoclinic, $a = 13.351(5)$, $b = 12.654(5)$, $c = 9.648(5)$ Å, $\beta = 100.201(5)$, $V = 1604(2)$ Å^3, $T = 93(2)$ K, space group $P2_1/c$, $Z = 4$, 13339 reflections measured, 2830 unique reflections ($R_{int} = 0.0395$). Final $R_1 = 0.0423$ ($I > 2\sigma(I)$), $wR(F^2) = 0.1081$ (all data). CCDC 927528.

    Crystal data for ***5****·(CH₃OH)₄:* $C_{31}H_{34}N_2O_4S_2$, $M = 562.72$, orthorhombic, $a = 26.9384(4)$, $b = 10.9791(2)$, $c = 9.7976(1)$ Å, $V = 2897.73(7)$ Å^3, $T = 100(1)$ K, space group $Pna2_1$, $Z = 4$, 12803 reflections measured, 5059 independent reflections ($R_{int} = 0.0294$). Final $R_1 = 0.0481$ ($I > 2\sigma(I)$), $wR(F^2) = 0.1347$ (all data). CCDC 927529.

    Crystal data for ***7****·CH₃OH:* $C_{32}H_{22}N_6OS_2$, $M = 570.68$, triclinic, $a = 7.255(2)$, $b = 13.009(3)$, $c = 15.508(4)$ Å, $\alpha = 102.06(2)$, $\beta = 94.34(2)$, $\gamma = 100.74(2)°$, $V = 1396.3(6)$ Å^3, $T = 93(2)$ K, space group $P\text{-}1$, $Z = 2$, 15275 reflections measured, 4939 unique reflections ($R_{int} = 0.0770$). Final $R_1 = 0.0788$ ($I > 2\sigma(I)$), $wR(F^2) = 0.2190$ (all data). CCDC 927530.

    Crystal data for ***9****·(CH₃OH)₂·CH₂Cl₂:* $C_{52}H_{48}Cl_2N_2O_2$, $M = 803.82$, triclinic, $a = 8.9947(4)$, $b = 14.9306(9)$, $c = 17.197(2)$ Å, $\alpha = 106.686(2)$, $\beta = 97.833(2)$, $\gamma = 103.917(2)°$, $V = 2094.3(2)$ Å^3, $T = 93(2)$ K, space group $P\text{-}1$, $Z = 2$, 36725 reflections measured, 7376 unique reflections ($R_{int} = 0.0446$). Final $R_1 = 0.0621$ ($I > 2\sigma(I)$), $wR(F^2) = 0.1930$ (all data). CCDC 927531.
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