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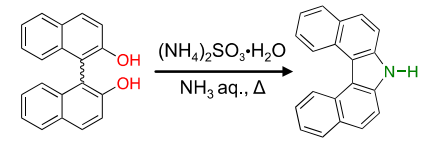

Racemic BINOL

DBC
Conversion: 99%
Isolated yield: 96%

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Fathy Hassan[a,b], Masuki Kawamoto*[,a,b,c,d], Krishnachary Salikolimi[a], Daisuke Hashizume[e], Takuji Hirose[b], and Yoshihiro Ito*[,a,c]

[a]*Emergent Bioengineering Materials Research Team, RIKEN Center for Emergent Matter Science (CEMS), 2-1 Hirosawa, Wako, Saitama 351-0198, Japan*
[b]*Graduate School of Science and Engineering, Saitama University, 255 Shimo-Okubo, Sakura-ku, Saitama 338-8570, Japan*
[c]*Nano Medical Engineering Laboratory, RIKEN, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan*
[d]*Photocatalysis International Research Center, Tokyo University of Science, 2641 Yamazaki, Noda, Chiba 278-8510, Japan*
[e]*Materials Characterization Support Unit, RIKEN Center for Emergent Matter Science (CEMS), 2-1 Hirosawa, Wako, Saitama 351-0198, Japan*

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ABSTRACT

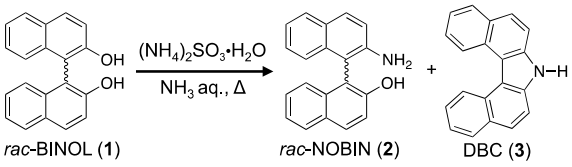
An operationally simple ring closure of racemic 1,1'-bi-2-naphthol (BINOL) yielded the heterocyclic aromatic compound 7*H*-dibenzo[*c*,*g*]carbazole (DBC). This one-pot method gave a good conversion and is suitable for gram-scale synthesis. DBC derivatives have high thermal durability, amorphous and crystalline structures with unique morphological properties, and semi-conducting behavior with potential applications in organic electronics.

7*H*-Dibenzo[*c*,*g*]carbazole (DBC) is a heterocyclic aromatic compound that is important in toxicology, pharmacology, and pharmaceuticals. DBC derivatives, which are used as standard reagents, show a broad range of biological and carcinogenic activities.[1] Exposure of various tissues, including skin, liver, lung, and stomach, to DBC has caused tumors in several experimental animals.[2] On the other hand, aromatic DBC compounds have recently attracted particular interest as semiconducting materials for organic light-emitting diodes (OLEDs).[3]

Despite the diverse applications of DBC derivatives, there are few efficient procedures for their synthesis. Lieber and co-workers synthesized DBC *via* lithium desulfurization of 7*H*-dibenzo[*c*,*h*]phenothiazine, with a yield of 33%.[4] The acid-catalyzed reaction of 2,2'-hydrazonaphthalene gave DBC in only 5% yield as a by-product with 2,2'-diamino-1,1'-binaphthyl (BINAM).[5] Alkylated DBCs can be obtained in low yield (~5%) by Fisher indole synthesis and subsequent dehydrogenation over chloronil or palladium on activated charcoal.[6] Recently, Lim and co-workers reported the acid-catalyzed condensation of BINAM to give DBC with a good yield of 85%.[7] However, commercially available DBC is still expensive (US$19.1 mg^{-1}, Sigma-Aldrich), therefore its practical use is limited.

In this study, we report that the one-step ring closure of 1,1'-bi-2-naphthol (BINOL) gives DBC with a 99% conversion. Simple heating of racemic BINOL (US¢0.3 mg^{-1}, Sigma-Aldrich) with $(NH_4)_2SO_3 \cdot H_2O$ and an aqueous ammonia solution (NH_3 aq.) in an autoclave results in condensation of the initially formed 2-amino-2'-hydroxy-1,1'-binaphthyl (NOBIN) to furnish DBC. The gram-scale synthesis of DBC, with an isolated yield of 96%, using this method represents a cost-effective one-pot procedure for DBC synthesis. *N*-Alkylated and *N*-arylated DBCs were also synthesized in order to explore their potential use as optoelectronic materials.

During a study of the amidation of racemic BINOL (**1**) to racemic NOBIN (**2**),[8] we found that DBC (**3**) was produced when **1** and the aminating reagent (AR) $(NH_4)_2SO_3 \cdot H_2O$ in NH_3 aq. (AR:NH_3 aq. = 1:2.6 mol/mol) were heated at 200 ºC in an autoclave (Scheme 1). The conversions of the resulting compounds were monitored using chiral high-performance liquid chromatography (HPLC); the elution times for **3**, (*R*)-**2**, and (*S*)-**2** were 6, 11, and 22 min, respectively. Isolated yields were determined after separation by recrystallization from benzene.



Scheme 1. Synthesis of DBC from *rac*-BINOL

Optimization of the reaction time and the **1**:AR ratio led to an increase in the conversion of **3** (Table 1 and ESI). Initially, the

* Corresponding author. Tel.: +81-48-467-2752; fax: +81-48-467-9300; e-mail: mkawamot@riken.jp (M. Kawamoto), y-ito@riken.jp (Y. Ito)

conversion of **3** was only 12% for **1**:AR = 1:10 (Entry 1). The conversion was improved upon increasing the **1**:AR ratio or reaction time (Entries 2 and 3). Adjustment of the reaction time and reagent ratio resulted in the conversion increasing from 12% (Entry 1) to 27% (Entry 4). Extending the reaction time from 6 d to 10 d led to the efficient formation of **3** (Entry 5). Increasing the **1**:AR ratio was effective for obtaining high conversions (Entries 5–7): a conversion of 81% was obtained using **1**:AR = 1:36 (Entry 7). However, the conversion gradually became saturated even when the amount of AR was increased. We suggest that this saturation is caused by AR consumption. For entry 8, one-half of the AR was used for the first 5 d, and then the remaining AR was added and the reaction continued for a further 5 d. This strategy gave a conversion greater than 90%. Almost complete reaction occurred in the presence of **1**:AR = 1:32 for 12 d, with a conversion of >99% and an isolated yield of 96% (Entry 9). Finally, increasing the reaction temperature to 220 ºC permitted the reaction time to be shortened to 8 d; the isolated yield was 96% (Entry 10).

Table 1. Optimization of the reaction conditions for **1** → **3**

Entry	Reaction time (d)	**1**:AR (mol/mol)	Conversion (%)[a]		Isolated yield (%)[b]	
			2	**3**	**2**	**3**
1	5	1:10	88	12	85	8
2	5	1:12	83	17	77	13
3	6	1:10	82	18	75	15
4	6	1:12	73	27	70	25
5	10	1:12	37	63	36	58
6	10	1:24	23	77	21	76
7	10	1:36	19	81	18	77
8	10	1:24[c]	6	94	4	90
9	12	1:32[c]	1	99	-[d]	96
10[e]	8	1:32[c]	1	99	-[d]	96

[a] Determined by chiral HPLC (ESI).

[b] After recrystallization from benzene.

[c] One-half of the AR was added for each half reaction time.

[d] Not determined.

[e] Reaction temperature: 220 ºC.

We then investigated the gram-scale synthesis of **3** using the experimental conditions outlined in entry 10. The reaction of **1** (3.0 g), $(NH_4)_2SO_3 \cdot H_2O$ (44.8 g), and NH_3 aq. (60 mL) in a 100 mL autoclave yielded **3** (2.7 g) with an isolated yield of 96%. This reaction method is suitable for large-scale synthesis; HPLC showed a high conversion of **3**, i.e., >99%. Furthermore, the purification step was simple. Because **3** was soluble in benzene, whereas **2** precipitated, further chromatographic separation was unnecessary. This one-pot process is expected to enable the efficient large-scale synthesis of DBC.

A possible mechanism for the ring closure reaction is shown in the ESI (Scheme S1). The first step is expected to be the amidation of **1** to **2** then ring closure of **2** to give **3** followed by the Bucherer carbazole reaction.[9] Electrophilic addition of a proton to the high electron density carbon atom in **2** gives resonance-stabilized proton adducts, addition of a bisulfite anion affords tetralonesulfonic acid to form tetraloniminesulfonic acids after amidation. Subsequently cyclization and elimination of sulfurous acid occurs to yield **3**.

We also examined the ring-closure behavior of **2** and its analogues (Fig. 1): *rac*-6,6'-dibromo-2-amino-2'-hydroxy-1,1'-binaphthyl (**2a**), and 2-amino-2'-hydroxy-1,1'-biphenyl (**4**) in order to clarify the reactivity of the DBC structure (Table 2). The reaction in the presence of **2**:AR = 1:24 (mol/mol) at 200 ºC for 10 d gave **3** with a conversion of 99% (Entry 1). The conversion decreased when **2** was reacted at 190 ºC for 10 d (Entry 2). The ring closure of compound **2a** under the same reaction conditions afforded 3,11-dibromo-7*H*-dibenzo[*c*,*g*]carbazole (**3a**) with a conversion of 60% along with unidentified compounds (7%) (Entry 3). The ring-closure reaction at 200 ºC yielded insoluble brown solids, resulting from thermal decomposition of **2a** (Entry 4). Thermogravimetric analysis (TGA) at a scanning rate of 10 ºC min^{-1} under nitrogen showed that the weight loss of **2a** at 200 ºC was 7.6%. In contrast, a weight loss of only 1.3% was observed for **2** at 200 ºC using the same scanning rate.

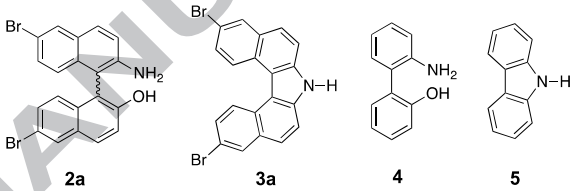


Figure 1. Structures of NOBIN analogues: **2a** and **4**, and their ring-closed structures: **3a** and **5**, respectively.

The ring closure of **4** to give 9*H*-carbazole (**5**) afforded mixtures; the conversions of **5** (45%), **4** (50%), and unknown compounds (5%) were obtained using HPLC analysis (Entry 5) (see ESI). These results suggest that the resonance structures of the proton adduct are essential for ring closure. A possible mechanism for this transformation is shown in the ESI (Scheme S2). Compound **2** gives four resonance structures, but only two resonance structures of **4** are involved in the synthesis of **5**. The low conversion of ring-closure may be the result of less resonance-stabilized proton adducts. In future studies, the ring closure of other NOBIN derivatives will be performed to clarify the reaction mechanism.

Table 2. Heterocyclic ring-closure of **2** and its analogues[a]

Entry	Starting material	Product	Reaction temperature (ºC)	Conversion (%)[a]
1	**2**	**3**	200	99
2	**2**	**3**	190	73
3	**2a**	**3a**	190	60
4	**2a**	[b]-	200	[b]-
5	**4**	**5**	200	45

[a] Reagents and conditions: starting material:AR = 1:24 (mol/mol), heated for 10 d in autoclave.

[b] Not observed.

Table 3. Thermal, optical, and electrical data for DBC derivatives

	T_{10} (ºC)	T_g (ºC)	T_c (ºC)	T_m (ºC)	λ_{max}^{abs} (nm)	λ_{max}^{em} (nm)	Φ_f[a]	HOMO (eV)[b]	LUMO (eV)	E_g (eV)[c]
3	322	28	-[d]	-[d]	277, 300, 347, 365	372, 391, 408 (sh)	0.66	-5.67	-2.45	3.22
6a	321	-2	78	113	282, 305, 352, 370	379, 394, 418 (sh)	0.42	-5.84	-2.62	3.22
6b	324	74	143	197	280, 305, 350, 367	376, 392, 413 (sh)	0.44	-5.62	-2.49	3.13
6c	363	-[d]	-[d]	235	278, 302, 347, 364, 380 (sh)	-[d]	< 0.001	-5.96	-3.36	2.60

[a] Quinine sulfate (Φ_f: 0.546 in 1 N sulfuric acid) as the standard.

[b] Determined using PESA.

[c] Obtained from Tauc plot.

[d] Not determined.

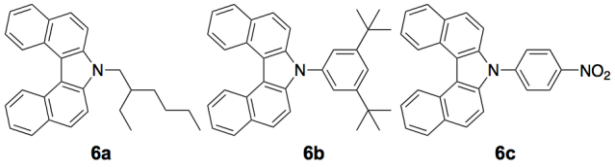


Figure 2. Molecular structures of *N*-alkylated and *N*-arylated DBC derivatives.

Next, we synthesized (see ESI for details) *N*-alkylated and *N*-arylated DBC derivatives (Fig. 2), and investigated their thermal, optical, and electrical properties (Table 3). TGA showed that **3** has high thermal stability: the 10%-weight-loss temperature (T_{10}) of **3** (322 ºC) was higher than that of **2** (269 ºC). The T_{10} values of *N*-(2-ethylhexyl)-DBC (**6a**, 321 ºC) and *N*-(3,5-di-*tert*-butylphenyl)-DBC (**6b**, 324 ºC) were almost the same as that of unsubstituted **3**. *N*-(4-nitrophenyl)-DBC (**6c**) had a higher T_{10} value (363 ºC), indicating that DBC derivatives are thermally stable, which is an advantage in the preparation of thin-film devices by vacuum deposition.[10] Differential scanning calorimetry (DSC) and X-ray diffractometry showed that the introduction of substituents at the nitrogen atom of DBC resulted in different morphologies. For compound **3**, an endothermic peak (ΔH: 19 kJ mol^{-1}) corresponding to the melting point (T_m) was observed at 159 ºC during the first heating cycle (Fig. 3a). Upon cooling to room temperature, the compound formed a transparent glass *via* a supercooled liquid state. We detected an endothermic event corresponding to the glass-transition temperature (T_g) at 28 ºC in the third heating cycle. The formation of a glassy state was also evident in the X-ray diffraction pattern. After thermal treatment above T_m, the diffraction pattern showed only a broad halo, indicating that the DBC unit was amorphous; this is because of steric hindrance due to the two non-planar naphthalene rings. The branched alkyl chain in **6a** gave rise to a decrease in T_g of −2 ºC. Upon further heating above the T_g, a broad exothermic peak at 78 ºC was identified as the crystalline temperature (T_c), as shown by sharp X-ray reflection peaks. Finally, the sample showed a T_m at 113 ºC. Compound **6b**, which contains a di-*tert*-butylphenyl group, had a higher T_g. The higher T_g arises from the rigid phenyl ring bonded to the nitrogen atom. The *N*-arylated structure also increases the T_c (143 ºC) and T_m (197 ºC) values, affording a thermally stable material.

Amorphous molecular materials enable the formation of thin films without grain boundaries, which are suitable for OLEDs.[11] To explore this molecular function, spin-coated films on fused-silica substrates were prepared (see ESI). The resulting amorphous thin films (film thickness: 80 nm) showed good transparency without light scattering, which is preferable for solution-processed device fabrication (Fig. 3b).

The DSC profiles show that compound **6c** gave a sharp peak corresponding to the T_m at 235 ºC (ΔH: 30 kJ mol^{-1}), without a T_g and T_c, in the third heating cycle. Needle-like single crystals of maximum average width 0.1 mm and length 6.5 mm were obtained using a liquid-phase crystal-growth method (Fig. 3c). Compound **6c** crystallized in the orthorhombic space group *Pbca* [a = 9.30318(18) Å, b = 16.8049(3) Å, c = 23.6779(4) Å] (Fig. 3d). The DBC unit was determined to have a dihedral angle (C2–C1–C12–C13) of 16.87(18)º. Furthermore, the 4-nitrophenyl unit at the nitrogen position led to a distorted structure with a dihedral angle (C26–C21–N1–C10) of 43.41(14)º. The molecular orientation was a head-to-tail arrangement of an electron-donating (D) group, i.e., DBC, and an electron-accepting (A) group, i.e., the 4-nitrophenyl unit. The intermolecular distance (C2–C26) between the D–A units was 3.4329(14) Å, which is similar to the sum of the van der Waals radii. These results suggest that π stacking of **6c** is crucial for the formation of a crystalline structure.

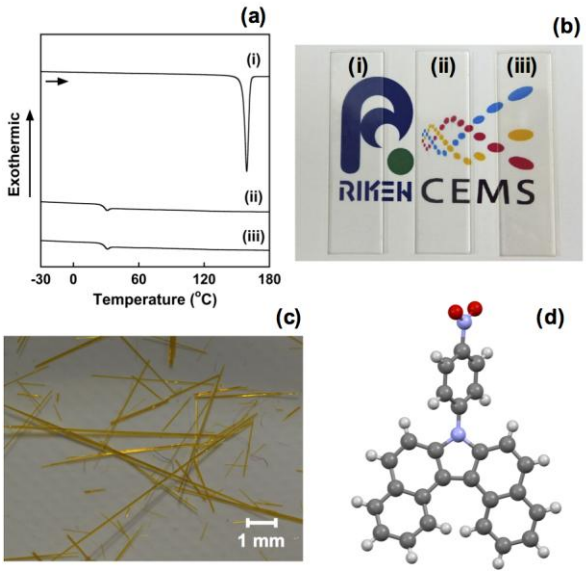


Figure 3. (a) DSC profiles of **3** in (i) first, (ii) second, and (iii) third heating cycles. Scanning rate: 10 ºC min^{-1}. (b) Spin-coated films of **3** (i), **6a** (ii), and **6b** (iii) on fused-silica substrate. (c) Single crystals of **6c**. (d) Crystal structure of **6c**.

Figure 4a shows the absorption spectra of the DBC derivatives in 1,4-dioxane. All the spectra indicate clear vibronic structures, consistent with the rigid structures. Compounds **3**, **6a**, and **6b** show an absorption peak at around 370 nm, corresponding to the 0–0 transition of the DBC unit. In contrast, the **6c** spectrum broadens at around 380 nm, which may be related to the D–A effect between the DBC and nitrophenyl groups. DFT

calculations show that the nitrophenyl group is involved in electron localization, resulting from the increased electron-withdrawing capability of the terminal unit.[12]

DBC showed fluorescence in 1,4-dioxane, with a fluorescence maximum (λ_{max}^{em}) at 372 nm, corresponding to a Stokes shift of 7 nm (Fig. 4b). The fluorescence spectra of *N*-alkylated **6a** and *N*-arylated **6b** showed similar λ_{max}^{em} values and Stokes shifts. The small Stokes shifts indicate that the annulated DBC structure is rigid, suggesting that changes in the molecular shape and size during photoexcitation are small.[13] Compound **3** gave a fluorescence quantum yield (Φ_f) of 0.66, using quinine sulfate as a standard. In contrast, **3c** showed fluorescence quenching (Φ_f: < 0.001) as a result of charge transfer between the electron-localized DBC and 4-nitrophenyl units.[14] Finally, the energy levels of the DBC derivatives were evaluated using absorption spectroscopy and photoelectron spectroscopy performed in air (PESA) (Table 3).

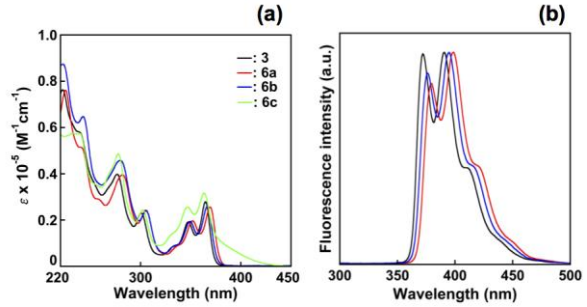


Figure 4. Absorption (a) and fluorescence (b) spectra of DBC derivatives in 1,4-dioxane. Fluorescence spectra were normalized at λ_{max}^{em} values.

Compared with **3**, **6a**, and **6b**, compound **6c** had a deep highest occupied molecular orbital (HOMO) level due to the electron-accepting nitrophenyl group, resulting in a lower electron-donating ability. The energy bandgaps (E_g) of the DBC derivatives were determined from Tauc plots,[15] and the lowest unoccupied molecular orbital (LUMO) levels were calculated by subtracting the E_g values from the relevant HOMO levels. The energy levels of DBC can be modulated by substituents at the nitrogen position, and electron-withdrawing groups are particularly effective for changing the electron-donating behavior.

In summary, we have achieved the heterocyclic ring closure of BINOL to DBC with a high conversion of 99%. This cost-effective method, with an isolated yield of 96%, was applicable for gram-scale synthesis. Furthermore, the DBC derivatives were found to have good thermal stabilities above 320 ºC. Crystallographic analyses indicate that DBCs show an amorphous or crystalline state, depending on the substituents. Their relatively high fluorescence quantum yields, i.e., 0.66, make them good candidates for fluorophores. Photoelectron spectroscopy shows that DBCs are semiconductors. These results suggest that the facile synthesis of DBC will enable the development of DBC materials for diverse applications especially for organic electronics.

Acknowledgments

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A. Supplementary data

Electronic Supporting Information (ESI) associated with this article can be found, in the online version, at https://doi.org/10.1016/j.tetlet.2017.XX.XX

Contains: Characterization data for all compounds, DSC and TGA profiles, XRD patterns, DFT calculation, PESA profiles, and Tauc plots (PDF).

CCDC-1573305 contains the crystallographic data for **6c**. The data can be obtained from The Cambridge Crystallographic Data Centre (CCDC) *via* www.ccdc.cam.ac.uk/data_request/cif.

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Highlights

- Heterocyclic ring closure of 1,1'-bi-2-naphthol yields 7*H*-dibenzo[*c*,*g*]carbazole.
- 7*H*-dibenzo[*c*,*g*]carbazole is obtained by simple heating in an autoclave.
- Gram-scale synthesis is useful in the development of optoelectronic materials.