A crystalline bisindolylmaleimide with strong solid-state fluorescence of red color and its analogous cross-linked polymer without fluorescence

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A crystalline bisindolylmaleimide (BIM) with strong fluorescence in the solid state was prepared and studied. Its analogous cross-linked polymer with the same BIMs fluorophore was designed and characterized. The investigation of the covalent bonding networking effect on the solid-state fluorescence was carried out by the comparison between 3 and 4.

1. Introduction

Organic fluorescent materials with strong emission in solid state are crucial in both fundamental research and industry applications. Although a number of organic molecules with strong emission in diluted solution have been reported, most of them become weakly luminescent or non-luminescent in the solid state. It is mainly owing to the aggregation caused by the strong intermolecular interaction between neighboring fluorophores. It is urgent to develop red fluorescent materials with high emission in solid state. Several efforts have been made to obtain intense fluorescence in the solid state, including the introduction of bulky substituents, introduction of non-planar structure, construct of dendrimer and cross-linked polymer network, J-aggregated formation, enhanced intramolecular charge transfer transition, and aggregation-induced emission.

Bisindolylmaleimides (BIMs) such as arcyriarubin A originally from natural products have attracted much attention as promising red fluorescent materials, owing to their special structure such as non-planar and D-A system. Nakazono et al. reported BIM small molecules with large Stokes shift and long-lasting chemiluminescence properties. Chow et al. reported BIM showing intensive red fluorescence and with quantum yield of 51% in acetonitrile. Tian et al. developed dye-sensitized solar cells (DSSC) based on BIMs. However, few studies on polymers containing BIM were carried out, especially when the solid-state fluorescent properties was concerned. And benzyl group was found to have positive effect in keeping the fluorescence of BIM. In addition, polymerization was usually done by noble metal-mediated coupling. It will be perfect for the development of materials if non-metal-catalyzed polymerization could be used.

In this communication, the red organic compound 3 based on the N,N'-dibenzylation of 2 with intensive emission in solid state was reported. In addition, its corresponding cross-linked polymer 4 based on the polymerization of 2 was prepared in order to investigate the influence of covalent bonding network on the solid-state fluorescence. To the best of our knowledge, this is the first example of cross-linked polymer containing BIM reported.

2. Experimental

2.1. Materials and instrumentation

Mesitylene, N-bromosuccinimide (NBS), benzoyl peroxide (BPO), aniline, benzyl bromide (BnBr), and N,N-dimethylformamide (DMF) were purchased from Sinopharm Chemical Reagent Beijing Co., Ltd., and used as received. Tetrahydrofuran (THF) was purchased from Sinopharm Chemical Reagent Beijing Co., Ltd., and distilled over sodium distilled from sodium and benzophenone immediately before use. Reactions were stirred using Teflon-coated magnetic stir bars. Analytical
TLC was performed with 0.20 mm silica gel 60F plates. Chromatographic purification of products was carried out by flash chromatography on silica gel (230–400 mesh).

Infrared spectra were recorded on a Nicolet 8700 Fourier transform spectrometer. Solution NMR spectra were measured in CDCl₃ (with TMS as internal standard) on a Bruker AV400 or Varian INOVA-400 M (¹H at 400 MHz, ¹³C at 100 MHz) magnetic resonance spectrometer. Solid-state ¹³C-CP/MAS NMR spectra were recorded on a Bruker Avance III 400 NMR spectrometer. The samples were spun at MAS rate of 5 kHz in all experiments. ¹³C NMR spectra were acquired using a cross-polarization pulse sequence with total suppression of side bands (CPTOSS) and a pulse length of 7.5 μs. Chemical shifts (δ) are reported in ppm, and coupling constants (J) are

**Figure 1.** The bisindolylmaleimide (BIM) 3 and its polymer 4.

**Figure 2.** The crystal structure (left) and intermolecular packing diagram (right) of 3.

**Figure 3.** FTIR spectra of 4 and related starting materials.
Figure 4. Solid-state $^{13}$C CP/MAS NMR spectra of 4.

Figure 5. TGA plots of compounds 1–4.

in Hz. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. High-resolution EI mass spectra (HR-EI-MS) were recorded on an GCT CA127 Micronass UK mass spectrometer. Thermogravimetric analysis (TGA) was performed in a TGA analyzer (TGA/DSC15F/417-2, Mettler Toledo) at heating rates of 10 °C/min from room temperature to 800 °C in a nitrogen atmosphere (40 mL/min). Nitrogen sorption isotherms were obtained with Micromeritics ASAP 2020 M + C accelerated surface area and porosimetry analyzers at 77 K. The samples were degassed overnight at 120 °C. The XRD patterns of the resulting samples were recorded on a X’Pert Pro MPD (PANalytical, The Netherlands) diffractometer with monochromatic Cu Kα radiation ($\lambda = 1.5406 \text{ Å}$) at 40 kV and 40 mA, the scanning speed was 0.01° s$^{-1}$, and the step size was 0.01° from 10° to 70°(2 h). Solid-state fluorescent spectra were measured in Hitachi F-4500 spectrophotometer, and absolute quantum yields were measured by Hamamatsu Photonics Quantaurus QY.

2.2. Preparation of 2 and 3

To an aqueous solution of KOH (10%, 1.3 mol, 1.3 equiv.) was added monomer 1 (3.27 g, 10 mmol, 1 equiv.), and
precipitate was filtered, washed with water to pH of 7, and
dried to give the anhydride (2.93 g, yield 90%). Rf = 0.4 [V (EtOAc)/V (petroleum ether) = 1/1]. IR (KBr, cm⁻¹): 3572 (m), 3394 (s), 3185 (w), 3055 (w), 2972 (w), 2931 (w), 1819 (m), 1743 (s), 1696 (w), 1614 (m), 1528 (s), 1491 (w), 1425 (s), 1334 (w), 1301 (w), 1250 (s), 1179 (m), 1128 (m), 1076 (w), 1037 (m), 922 (w), 877 (w), 847 (w), 814 (w), 743 (s), 653 (s), 652 (w), 599 (w). The anhydride was used directly for the
next step. The mixture of anhydride 1 (328 mg, 1 mmol,
1 equiv.) and aniline (1.2 g, 13 mmol, 13 equiv.) in AcOH
(10 ml) was heated at reflux for 3 h. The reaction was
stopped and cooled to RT, and quenched with HCl (10 N,
10 ml) to give the compound 2 as red solid (306 mg,
yield 76%). Rf = 0.59 [V (EtOAc)/V (petroleum ether) = 1/1]; 1H-NMR (400 MHz, DMSO-d₆) δ (ppm): 11.73 (s, 2H), 7.81 (s, 2H), 7.39–7.55 (m, 7H), 7.0 (t, J = 7.6 Hz, 2H), 6.88 (d, J = 8.0 Hz, 2H), 6.66 (t, J = 7.6 Hz, 2H); IR (KBr, cm⁻¹): 3400 (m), 3335 (w), 3283 (m), 1761 (m), 1699 (s), 1603 (w), 1522 (m), 1485 (w), 1456 (w), 1418 (s), 1340 (w), 1321 (w), 1241 (m), 1184 (w), 1164 (w), 1114 (w), 1096 (m), 1043 (w), 903 (m), 827 (w), 794 (w), 744 (m), 618 (w), 591 (w), 558 (w). HR-MS (ESI): m/z 426.1191; [M + Na⁻]⁺ (C₂₆H₁₇N₃O₂Na⁺, Calcd 426.1213), 442.0931; [M + K⁺]⁺ (C₂₆H₁₇N₃O₂K⁺, Calcd 442.0952).

To an ice bath-cooled suspension of NaH (60%, 120 mg,
3 mmol, 3 equiv.) in DMF (10 ml) under N₂ was added a
solution of 2 (403 mg, 1 mmol, 1 equiv.) in DMF (10 ml)
dropwise; the resulting mixture was stirred for 30 min and
then treated with BnBr (342 mg, 2 mmol, 2 equiv.). After
being stirred at RT for 2 h, TLC showed completion of the
full conversion of 2. The reaction mixture was quenched
with sat. NH₄Cl (10 ml), extracted with EtOAc (3 x 20 ml),
the combined organics were dried over anhydrous Na₂SO₄,
concentrated, and the residue was passed through silica
gel [eluted with V (CH₂Cl₂)/V (petroleum ether) = 1/10] to
give compound 3 as a red solid (407.4 mg, yield 98%).
Rf = 0.66 [V (ethyl acetate)/V (petroleum ether) = 1:2];
1H-NMR (CDCl₃, 400 MHz) : δ (ppm): 7.78 (s, 2H), 7.49 (t,
was quenched with sat. NH₄Cl (10 ml), and the resulted red solid was filtered and washed with water. The crude product was soxhlet abstracted with distilled water, MeOH, and THF, respectively, for 20 h, then dried at 120 °C for 18 h under vacuo to give final product 4 (518 mg, yield 72%). 13C CP/MAS NMR (400 MHz): δ (ppm) 170.6, 136.8, 127.5, 107.5, 49.8. IR (KBr, cm –1): 3048(w), 1759(w), 1705(s), 1606(w), 1530(m), 1500(m), 1462(m), 1381(s), 1248(w), 1175(m), 1116(w), 1086(w), 1019(w), 739(m), 691(w), 634(w).

3. Results and discussions

Although it is commercially available, arcyriarubin A (1) was made in 10-gram scale starting from indole by following the known procedure.[37] Compound 1 was treated with aqueous KOH to give anhydride 5 in 90% yield, which was transferred to compound 2 in 80% yield via the reaction of anhydride 5 with excess aniline in the presence of AcOH (Scheme 1). 1,3,5-tribromomethylbenzene (6) was used very often in the development of materials and...

**Scheme 1. The synthesis of 3 and 4.**

**Table 1. Crystal data of compound 3.**

| Parameters                                      | Compound 3                  |
|------------------------------------------------|-----------------------------|
| CCDC deposit number                            | 1056839                     |
| Empirical formula                              | C₄₀H₂₉N₃O₂                   |
| Formula weight                                  | 583.66                      |
| Temperature (K)                                 | 113                         |
| Crystal system                                  | triclinic                   |
| Space group                                     | P-1                         |
| a (Å)                                          | 8.6769(17)                  |
| b (Å)                                          | 13.2413(3)                  |
| c (Å)                                          | 13.6033(3)                  |
| α (°)                                          | 82.8027(72)                 |
| β (°)                                          | 79.3966(69)                 |
| γ (°)                                          | 84.0141(72)                 |
| Volume (Å³)                                     | 1518.8(5)                   |
| Z                                               | 2                           |
| ρ calc (g/cm³)                                  | 1.276                       |
| Radiation                                       | Mo Kα (λ = 0.7107)          |
| Final R indexes [{ > 2σ (I)}]                   | R1 = 0.0394, wR2 = 0.0881   |
| Final R indexes [all data]                     | R1 = 0.0714, wR2 = 0.1113   |

J = 6.4 Hz, 4H), 7.22–7.37 (m, 10H), 7.14 (d, J = 6.4 Hz, 4H), 7.05 (t, J = 7.2 Hz, 4H), 6.75 (t, J = 8.0 Hz, 2H), 5.35 (s, 4H); 13C-NMR (150 MHz, CDCl₃) δ (ppm): 171.2, 136.6, 136.5, 132.6, 132.4, 129.1, 129.0, 128.0, 127.4, 127.1, 127.0, 126.6, 126.4, 122.6, 122.4, 120.4, 110.1, 106.4, 50.7; IR (KBr, cm⁻¹): 2923(s), 2852(m), 1816(w), 1751(s), 1702(m), 1529(s), 1460(w), 1383(m), 1252(m), 1172(m), 911(w), 800(w), 738(m), 695(w); HR-MS (MALDI): m/z 583.2251 [M]+ (C₄₀H₂₉N₃O₂⁺, Calcd 583.2260).

2.3. Preparation of 4

To an ice bath-cooled suspension of NaH (60%, 160 mg, 4 mmol, 4 equiv.) in DMF (10 ml) under N₂, was added a solution of BIM 2 (604.5 mg, 1.5 mmol, 1.5 equiv.) in DMF (10 ml) dropwise; the resulting mixture was stirred for 30 min and then treated with 1,3,5-Tribromomethylbenzene (357 mg, 1 mmol, 1 equiv.) in DMF (5 ml). After being stirred at RT for 2 h, TLC showed completion of the full conversion of starting materials, and some red solid precipitated. The reaction was quenched with sat. NH₄Cl (10 ml), and the resulted red solid was filtered and washed with water. The crude product was soxhlet abstracted with distilled water, MeOH, and THF, respectively, for 20 h, then dried at 120 °C for 18 h under vacuo to give final product 4 (518 mg, yield 72%). 13C CP/MAS NMR (400 MHz): δ (ppm) 170.6, 136.8, 127.5, 107.5, 49.8. IR (KBr, cm⁻¹): 3048(w), 1759(w), 1705(s), 1606(w), 1530(m), 1500(m), 1462(m), 1381(s), 1248(w), 1175(m), 1116(w), 1086(w), 1019(w), 739(m), 691(w), 634(w).
was here synthesized in 23% yield by slightly modifying the known procedure.[38] It is worth mentioning that the preparation could be achieved using 1,2-dichloroethane other than benzene used in the literature, which would be safer for practitioners. Prior to the polymerization of monomer 2 with 6, we investigated relevant model reaction to evaluate the reactivity of N–H group with benzylbromide in the presence of NaH. The reaction of compound 2 with 2 equivalents of benzylbromide in DMF gave compound 3 in 98% yield (Scheme 1). The reaction was monitored by TLC, which showed spot-to-spot conversion from starting material to a less-polar product. In the 1H-NMR spectrum of 2, the characteristic peaks attributable to NH group were observed at 11.73 ppm (see Figure S1 in supporting information), which disappeared after the reaction. In the IR spectrum of 2, a strong peak attributable to indole’s NH (λ max 3360 cm−1) was observed, which disappeared after N-benzylation to give 3.

The structure of 3 was confirmed by FT-IR, NMR, and high-resolution mass spectrum (see Figures S3–6). This is the strong evidence for the full conversion of NH. In the 13C-NMR spectrum, a signal attributable to carboxyl of imide at 171.2 ppm, the peaks in the region of 100–135 ppm assigned to sp2 carbons of indole and phenyl rings as well as methylene attached to N of indole were seen, which is the evidence for the existence of bisindolylmaleimide. In addition, the high-resolution mass spectrum of 3 gave the peak of 426.1191 [M + Na]+ (C26H13N2O2Na+, Calcd 426.1213), confirming the right structure of 3.

The structure of compound 3 (Figure 2) was further confirmed by X-ray diffraction analysis on its single crystal, which was obtained by the evaporation of solvents. It is clear that the two indole rings are not coplanar, but have a dihedral angle of 39.6°. The dihedral angle between two indole rings and maleimide amounts to 33.5°. And the two indole rings are antiparallel, which leads the two benzyl groups extend away from the BIMs core. The N-phenyl and maleimide ring are also non-planar, with a dihedral angle of 49.5°. The molecular configuration of 3 in crystal seems like a 'pyramid'.[39] The maleimide is in the peak of the tower, the two indole rings are the side face, and the two benzyl groups are the underside. Crystal parameters and refinement data are listed in Table 1. The crystal packing is indicated in Figure 2.

From the intermolecular packing diagram, it can be seen that the maleimide ring of one molecule was parallel to the two neighboring maleimide rings, and the centroid-to-plane distance between the two neighboring maleimide rings are measured to be 8.67 Å (see Figure S9 in supporting information). The same value was measured for indole rings. Between the two maleimide rings, the N-phenyl ring was located; the dihedral angles amount to 49.5° and centroid-to-plain distance of 3.56 Å. These interactions can be deemed poor interaction.

The absorption and fluorescent spectra of compound 3 were recorded in THF (see Figures S7–8). The absolute photoluminescence quantum yields of 3 in THF were estimated to be 61.9%. The photoluminescence quantum yields of 3 were estimated to be as high as 54.6% in the solid state, which could be the result of the non-planar and pyramid-like configuration for preventing fluorescence quenching, as shown in crystal packing diagram.

Based on this result, we wonder if it is impossible to introduce networking by covalent bond formation to keep or even strengthen the solid-state fluorescence. The monomer 2 was treated with 1.5 equiv. of 1,3,5-tribromomethylbenzene (at room temperature for 2 h, and cross-linked polymer 4 was prepared smoothly in a yield of 72%, after routine work-up. The comparison between compound 2, monomer 3, and their corresponding cross-linked polymer 4 is shown in Figure 3.

In the FT-IR spectra, a characteristic peak of N–H (3300–3500 cm−1) was seen in the starting material of 2, and a peak of C-Br (528–575 cm−1) was observed in 6. The absence of the above two peaks in the IR spectra of polymer 4 revealed the disappearance of N–H and C–Br bond, i.e., the completeness of the N-benzylation was achieved, which was similar to model compound 3. And strong peaks in the region of 1700–1800 cm−1 imply the presence of bisindolylmaleimide moiety.

As the cross-linked polymer was not dissolved in solvents, solid-state CP/MAS NMR spectrum was used to characterize polymer 4. The comparison of 13C-NMR spectra between polymer 4 and its related monomer 3 is shown in Figure 3.

In the solid-state 13C CP/MAS NMR spectrum (Figure 4), a signal attributable to carbonyl of imide at 170.6 ppm and a signal attributable to methylene at 49.8 ppm were observed. Besides, signals attributable to phenyl and indole rings as well as double bonds of maleimides were observed in the region of 90–140 ppm. Besides, the elemental analysis on polymer 4 showed C, N, and H contents were supersimilar to its theoretical values (Table S1).

The thermal stability is an important parameter of materials to their application. And the TG analysis on all the compounds were carried out under N2 atmosphere at heating rate of 10 °C/min, as shown in Figure 5.

The data obtained from TGA are listed in Table S2. Compared to 1 and 2, which have T 5% temperature of 338 and 355 °C, the N-benzylated compound 3 gave T 5% temperature of 378 °C, T max of 452 °C, i.e., the N-benzylation of BIM increased the thermal stability with N–H substituted by N–Bn. The introduction of cross-linked polymer backbone contributed to higher T 5% temperature of 400, and 471 °C for T max. As far as the residue weight percentage is
concerned, the arcyriarubin A (1) has remaining weight percentage of 35%, and compounds 2 and 3 had lower residue weight percentage of 15 and 19%. The introduction of cross-linked polymer backbone increased the residue weight percentage to 55% at 800 °C. The thermal stability of BIMs at high temperature could be the result of their solid-state structures. In the crystal structure of 3 (Figure 2), the indolyl groups are oriented anti to each other.

In room light as well as irradiated at 365 nm, compound 3 was bright red powder, while their corresponding cross-linked polymer 4 was dark red powder, as indicated in Figure 6. The solid-state fluorescence spectra were recorded using Hamamatsu Photonics Quantaurus QY, and the absolute fluorescence quantum yield was measured to be less than 0.3%, which was much less than 54.6% of compound 3.

In order to get some understanding on why polymer 4 lost the fluorescence in solid state, the powder X-ray diffraction (PXRD) on 4 was carried out, since arrangement of molecules plays important role in the fluorescence. The PXRD was used to determine the state of compound 3 and its analogous polymer 4, and the comparison between 4 and 3 is indicated in Figure 7.

The PXRD patterns of polymer 4 and compound 3 are distinctly different. Compound 3 was crystalline based on the sharp peaks, but polymer 4 was amorphous based on the broad peaks.

In order to get the porosity information for amorphous polymer 4, the N2 absorption experiments were carried out at 77 K (Figure 8).

Polymer 4 showed small absorption toward N2. The hysteresis loops were seen in high-pressure area, which may be the result of interpenetration of the backbone and partially tectonic collapse. One explanation is that 6 has more soft CH2 moiety in the structure, which lead to interpenetration during the formation of polymers’ structure. The specific area of 4 was 43.36 m2 g−1 and the broad pore width from 15 to 100 nm. The low BET specific surface could be the result of close packing of subunits, which was proposed to be related with soft methylene (CH2) moiety in the cross-linked polymer, i.e., BIMs interpenetrated with each other during the formation of the cross-linked polymer, forcing the close packing of indole rings. In space, with the non-planar indole rings close to each other, the strong π–π stacking leads to quenching of fluorescence.

4. Conclusions

The bisindolymaleimides 3 derived from arcyriarubin A as well as their analogous cross-linked polymer 4 were synthesized in high yield. Their chemical structures as well as properties were investigated. Compound 3 gave photoluminescence quantum yield as high as 54.6%, owing to the non-planar and pyramid-like configuration for preventing fluorescence quench, while its analogous cross-linked polymer 4 showed low quantum yield in solid state, which may be caused by close packing during the formation of cross-linked polymer. The further effort to get fluorescent cross-linked polymer in solid state using more rigid building block is ongoing, which will be reported in due course.

Disclosure statement

No potential conflict of interest was reported by the authors.

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