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Boron(III)-Containing Donor–Acceptor Compound with Goldlike Reflective Behavior for Organic Resistive Memory Devices

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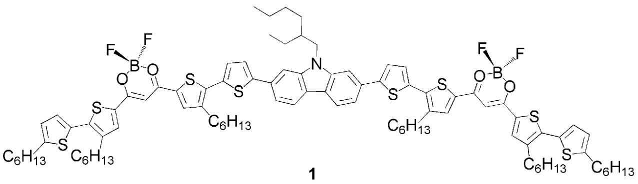
Abstract: *A small-molecule-based boron(III)-containing donor–acceptor compound has been designed and synthesized. Interesting goldlike reflective behavior was observed in the neat thin-film sample from simple spin-coating preparation, which can serve as a potential organic thin-film optical reflector. The small thickness in nanometer range and the relatively smooth surface morphology, together with simple preparation and easy solution processability, are attractive features for opening up new avenues for the fabrication of reflective coatings. Moreover, this donor–acceptor compound has been employed in the fabrication of organic resistive memory device, which exhibited good performance with low turn-on voltage, small operating bias, large ON/OFF ratio, and long retention time.*

Push-pull chromophores have attracted enormous interests in the scientific community because of their interesting photophysical, photosensitizing, and nonlinear optical properties.[1] In recent decades, this kind of compounds has drawn a lot of attention in material science because of their capability to function as photosensitizers and optoelectronic materials with facile modification of the HOMO and LUMO energy levels. A typical organic push-pull chromophore consists of an electron donor and an electron acceptor connected by a π-conjugated spacer.[2] By the judicious design and suitable choice of the donor and acceptor pair, desirable photophysical and photochemical properties can be achieved and have been widely applied in organic photovoltaics (OPVs)[3] and organic light-emitting diodes (OLEDs).[4]

More interestingly, compounds composed of donor–acceptor systems have rarely been reported to exhibit goldlike metallic-luster behavior.[5] Although there is no precise conclusion on the origin of the metallic-luster behavior in organic compounds, it has been proposed that such highly reflective behavior, mainly found in crystals, originates from the presence of both donor–acceptor systems and strong π–π stacking character. By utilizing the metallic luster of these organic compounds, it is believed that a new class of optical reflectors can be achieved by simple spin-coating or vacuum deposition preparation.

Besides that, in the past decade, there has been an increasing interest in the functionalization of organic-based materials consisting of a donor–acceptor couple for the fabrication of organic resistive memory devices.[6] In contrast to the traditional silicon-based memory devices, which are based on the amount of charges stored in the devices, the memory effect in organic memory devices is based on the electrical bistability of conductance (resistance), wherein a low-conductance state (OFF) is switched to a high-conductance state (ON).[7] Donor–acceptor couples have been demonstrated as promising candidates[8] to achieve electrical bistability through electric-field-induced charge transfer in conjugated compounds.

Recently, boron(III)-based materials have attracted a lot of attention in the field of optoelectronic and anion sensing applications because of the enriched photophysical properties.[9] In particular, boron(III) diketonates have been reported as active components in multidisciplinary areas, including luminescence,[10] nonlinear optics,[11] anion sensing,[12] and supramolecular self-assembly.[13] However, there is still a lack of research and understanding of the development of boron(III) diketonate-containing donor–acceptor compounds for various optoelectronic applications. As an extension of our continuing interests in designing various functionalized boron(III)-based materials,[14] we believe that by introduction of unique electron-accepting and electron-transporting boron(III) diketonates in push-pull chromophoric systems, new classes of materials having novel properties can be readily obtained. Herein, we report the synthesis of a donor–acceptor compound (**1**) containing boron(III) diketonate moieties as electron acceptor and a dithienyl-substituted carbazole as an electron donor, and the compound has been employed in the fabrication of organic resistive memory devices with good performances. More interestingly, this compound displays goldlike reflective behavior in thin films by simple spin-coating preparation, which can act as potential candidate for optical reflectors.



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The target compound **1** can be facilely synthesized through a double Stille cross-coupling between $Th_2acacBF_2ThBr$[15a] and $Carb(ThSnMe_3)_2$[15b] by using standard anaerobic reaction conditions[14h] (see Scheme S1 in the

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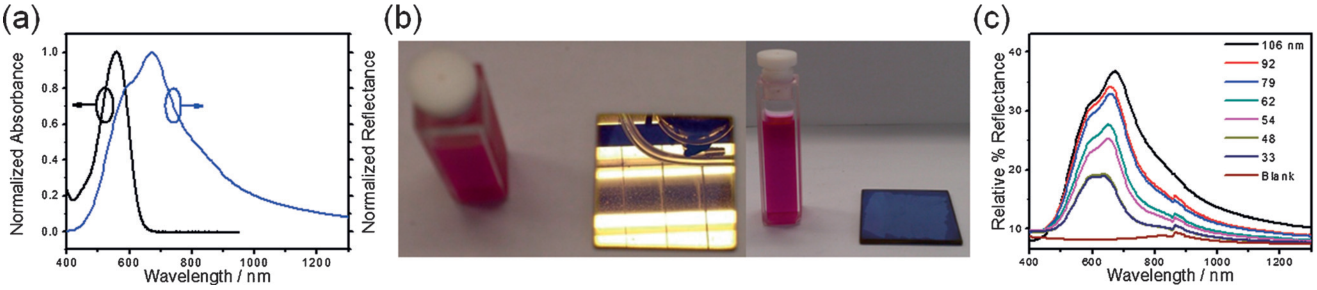

Figure 1. a) Normalized absorption spectrum of **1** in dichloromethane (black) and the normalized reflectance spectrum (blue) of the thin-film sample of **1**. b) Left panel: Image of a solution of **1** in dichloromethane (left) and a thin film of **1** coated onto a quartz plate exhibiting goldlike reflective behavior by showing the reflected image from a fluorescent lamp (right) viewed from the top; right panel: image of a solution of **1** in dichloromethane (left) and a thin film of **1** coated on quartz plate (right) viewed from the side. c) Relative reflectance spectra of a thin film of **1** coated on quartz plate at different thickness.

Supporting Information) to give an air-stable dark-purple compound. The identity of **1** has been confirmed by ^{1}H, ^{13}C{^{1}H}, ^{19}F{^{1}H}, and ^{11}B{^{1}H} NMR, as well as high-resolution MALDI-TOF mass spectrometry and elemental analysis.

Because of its long alkyl chains, **1** is soluble in most common organic solvents, for example, chlorinated solvents, toluene, and THF, except for alcoholic solvents. In a dichloromethane solution, **1** shows a deep-purple color, with an intense absorption band at $\lambda = 560$ nm ($\varepsilon_{\max} = 114\,000$ dm^{3} mol^{-1} cm^{-1}), as shown in Figure 1 a, and exhibits a very weak emission at about $\lambda = 670$ nm. Strong red luminescence at $\lambda = 617$ nm ($\phi = 0.35$, $\tau = 1.47$ ns) is observed when toluene is used as the solvent medium, suggestive of the charge-transfer character of **1**. Solvent-dependent studies were pursued to further investigate the spectroscopic origin of **1** (see Figure S1), with the emission energy well correlated to the Dimroth's solvent parameter[16a] (see Figure S2). Positive solvatochromism was observed with polar solvents causing a red shift in the emission band, supportive of the charge-transfer character of the emissive state. The Lippert–Mataga equation[16b] was employed to analyze the solvent dependence of the absorption and emission bands. By plotting the Stokes shift versus the orientational polarizability of the solvent[16b] (see Figure S3), **1** shows good linearity with a slope of 3116 cm^{-1} ($R^2 = 0.984$). This represents the presence of a large excited state dipole moment, which is indicative of the charge-transfer character from the carbazole donor to the boron(III) diketonate acceptor. **1** can be spin-cast into uniform thin films from a chloroform (or toluene or chlorobenzene) solution. Interestingly, goldlike reflective behavior has been observed in the neat thin-film sample when viewed from the top (Figure 1 b). Quantitative reflectance measurements were performed on a UV-vis-NIR spectrophotometer equipped with an integrating sphere. The normalized reflectance spectrum is shown in Figure 1 a and is compared to the normalized absorption spectrum in solution. A broad reflective range is observed from $\lambda = 450$ to 1300 nm, with peak reflectivity at $\lambda = 668$ nm (37 %), while the onset of the absorption spectrum is only at about $\lambda = 685$ nm. Moreover, the reflectance spectrum of a thin film of **1** was compared with that of an electron-beam-evaporated gold film of similar thickness (see Figure S4), which showed that the reflective range of the thin film of **1** is similar to that of the gold film while the relative percentage of the reflectance of the gold film is about twice in value to that of the thin film of **1**. The reflectivity was found to be sensitive to the thickness of the thin film, in which the percentage reflectivity is found to be enhanced from 18 to 37 % by increasing the thickness of the film (Figure 1 c). In addition, angle-dependent reflectance spectra of the thin film of **1** from 20° to 45° on a quartz plate were measured[16] (see Figure S5). A slight increase in the relative percentage of reflectance with almost no observable change in reflectivity profile was obtained, which is in sharp contrast to reflectance from liquid-crystal phases,[17] in which the reflectivity is highly angle-dependent, indicative of the unique reflectivity nature of **1** with goldlike reflective behavior.

X-Ray diffraction was employed to investigate the molecular packing of thin films of **1**, and the X-ray diffraction patterns for a thin-film of **1** are shown in Figure 2 a. The thin-film form of **1** exhibits an intense diffraction peak at 3.0° and a weak diffraction peak at 7.0°, which correspond to d spacings of 29.65 and 12.67 Å, respectively. A broad signal from 15.2 to 29.5° with a maximum at 21.1°, which corresponds to a d spacing of 4.06 Å, has been observed in the neat film. The d spacing of the broad signal is from 5.83 to 3.03 Å, suggestive of admixtures of pronounced intermolecular π–π stacking and alkyl–alkyl interactions in the thin-film sample. Similar X-ray diffraction patterns have been reported in polymers having a goldlike metallic luster,[5a,b] indicating that **1** exhibits similar molecular packing when compared with the previously reported polymers.[5a,b] Moreover, the surface morphology has been studied by atomic force microscopy (AFM; Figure 2 b), which shows the tapping-mode AFM topography and the corresponding cross-section profile of the AFM topographic image. The root-mean-square (RMS) roughness is found to be about ±2.8 nm, indicative of a relatively smooth surface morphology. Strong π–π interactions are believed to contribute to the smooth surface of **1**, in which molecules with strong π–π interactions can facilitate better molecular packing and film formation, resulting in a smoother surface, as revealed by the XRD pattern.

Further study by SEM has been made and the image of the surface of the thin film coated with **1** on a quartz plate is shown in Figure 2 c. A plain structureless image has been observed, suggestive of a smooth surface on the thin film.

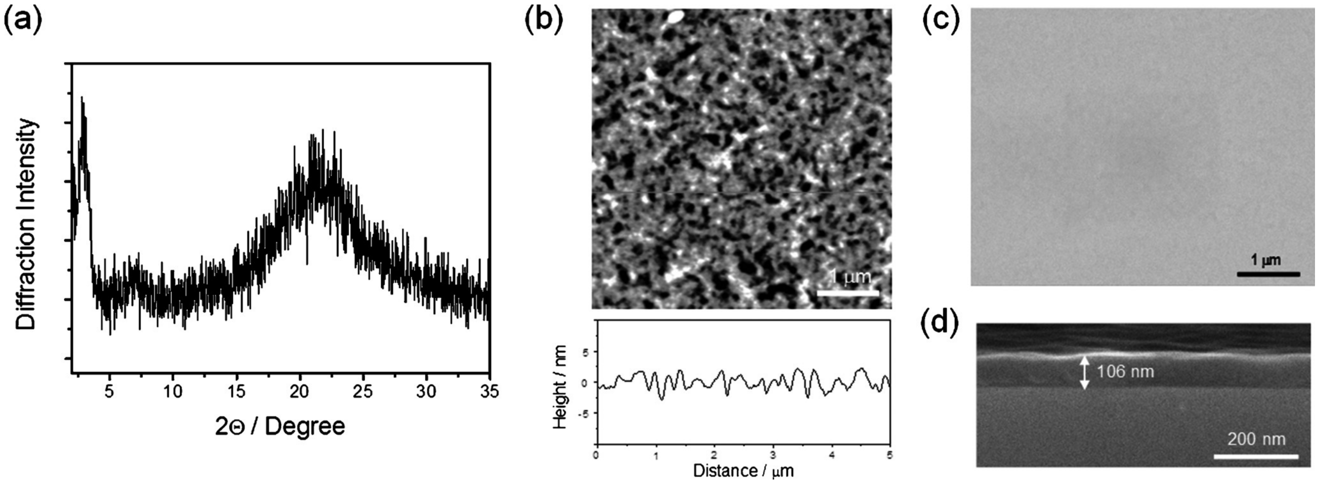

Figure 2. a) X-Ray diffraction pattern of thin-film sample of **1**. b) Tapping-mode AFM topography and the corresponding cross-section profile of AFM topographic image of the surface on the thin film coated with **1** on quartz plate (500 rpm). c) SEM image of the surface of the thin film coated with **1** on quartz plate (500 rpm). d) SEM image of the cross-section on the thin film coated with **1** on quartz plate (500 rpm).

Figure 2d shows the SEM image of the cross-section of the thin film, which is found to be about 106 nm, indicating that only a very thin film of active component in nanometer range is required for such high reflectivity. Recently, Bragg reflectors (dielectric mirrors) and photonic crystals for use as optical reflectors or filters have been studied extensively.[18,19] However, Bragg reflectors require multilayer preparation, where the layers are composed of materials of different refractive indices,[18] while three-dimensional architecture is essential for optical reflectors based on photonic crystals.[19] Unlike them, only spin-coating is required for **1** to serve as an optical reflector. In addition, from our results, optical reflectors that are composed of the present organic system, having metallic-luster behavior, confer advantages in being smooth in surface morphology and very thin, which is in contrast to the rough surface of photonic crystals and the multilayer thickness of Bragg reflectors. To the best of our knowledge, such behavior is extremely rare for small molecules and has not been reported for either small molecules or polymers with film thickness of around 100 nm. Further investigations for a better understanding of the principle and the controlling factors governing the reflectivity properties of the organic system with metallic-luster behavior are important and are in progress.

1 has also been employed in the fabrication of organic resistive memory devices to illustrate the potential application of boron(III) diketonate-containing donor–acceptor compounds as active components for organic memory devices. The device has a simple structure consisting of a film of **1** sandwiched between an indium-tin oxide (ITO) electrode and an aluminum electrode (Figure 3a). The film thickness of **1** and aluminum is found to be about 120 nm and 74 nm, respectively, from the SEM image of a cross-section of the device (Figure 3b). The memory behavior has been determined from the current–voltage performances of the as-fabricated device of Al/**1**/ITO (Figure 3c). The first sweep of the as-fabricated device exhibits an abrupt increase in the current at the switching threshold voltage (about 2.8 V). This process demonstrates the transition from a low-conductivity state, denoted “OFF”, to a high-conductivity state, denoted

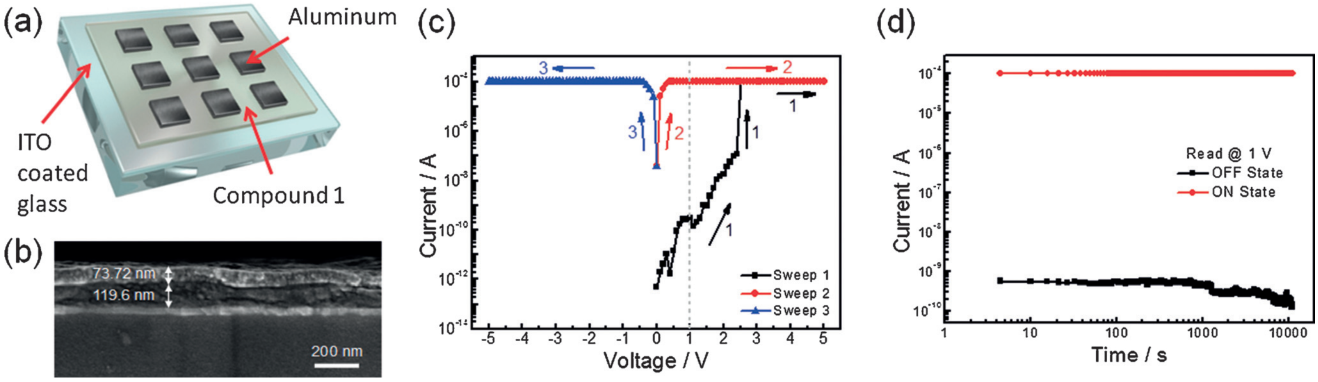

Figure 3. a) Illustration of the memory device composed of **1**. b) SEM image of a cross-section of the device. c) Current-voltage characteristics of an ITO/**1**/Al devices. d) Retention time of the ITO/**1**/Al devices in OFF and ON states under a constant stress (1.0 V).

"ON". The high-conductivity state is maintained during the second sweep of the device over a voltage range of 0 to 5 V. The device shows good stability in the ON state upon applying a reverse bias in the third sweep. In addition, it is worthwhile to note that the ON state can be relaxed to the OFF state after the power is turned off, and then changed to the ON state again by applying a bias, suggestive of the "static random-access memory" (SRAM) type of memory.[6] These processes can be repeated many times, and **1** is stable upon increase in voltage and the memory behavior is not a result of the decomposition of the active material. The stability of the device under a constant stress at 1 V is shown in Figure 3 d. No significant degradation is observed in current for the OFF and ON states for at least 10^4 seconds during the measurement, suggesting that the device exhibits a good stability and a precise control of the two independent states with low misreading rate. The two states exhibit a distinct current ratio of $1{:}10^7$ for the OFF and ON states, and is indicative of a high ON/OFF ratio, as shown in Figure S6. Also, the batch-to-batch device performances have been investigated by studying 15 individual devices (see Figure S7). The threshold voltage of the ON state is found to range from 2.8 to 3.4 V, indicative of a good repeatability.

To understand the energy states of **1**, the electrochemical properties of **1** have been studied by cyclic voltammetry (see Figures S8 a and S8 b). One quasi-reversible oxidation couple at +0.96 V ($\Delta E_p = 66$ mV) vs. SCE, and one quasi-reversible reduction couple at −0.74 V ($\Delta E_p = 60$ mV) vs. SCE are observed. The first reduction couple is tentatively assigned as the reduction of the diketonates.[14b,f] On the other hand, the first oxidation couple is assigned as dithienyl-substituted carbazole oxidation.[15b] The energy levels of the HOMO and the LUMO are found to be −5.18 and −3.48 eV, respectively, by using a ferrocenium/ferrocene couple as an internal reference. The energy band gap is determined to be 1.70 eV, which is similar to that determined from the UV-vis study (onset of lowest absorption band = 1.80 eV). Based on the results obtained from cyclic voltammetry, the energy barriers for hole injection and electron injection are found to be 0.38 and 0.82 eV, respectively, which are determined by the corresponding energy difference between the work function of the ITO electrode (−4.8 eV) and the HOMO level of **1** and between the work function of Al electrode (−4.3 eV) and the LUMO level (Figure 4). These results suggest that the hole injection is an energetically favorable process. On the basis of our findings, the mechanism of field-induced conductivity is proposed to involve an applied bias-controlled charge-transfer process. At a low voltage bias, low conductivity is observed because the energy is insufficient to overcome the injection barrier. When the applied bias reaches the threshold voltage, the charge carrier can be injected from the dithienyl-substituted carbazole to the diketonates. Such field-induced conductivity is believed to dominate in organic memory devices composed of donor–acceptor couples.[6] Unlike our previous study in which multiple states can be introduced through the use of the benzothiadiazole donor,[14h] the present work demonstrates that a variation in the donor group from benzothiadiazole to carbazole can lead to unique functional properties, indicating that the donor group plays an important role in governing the charge-trapping state which can be achieved through rational molecular design and judicious choice of the donor core.

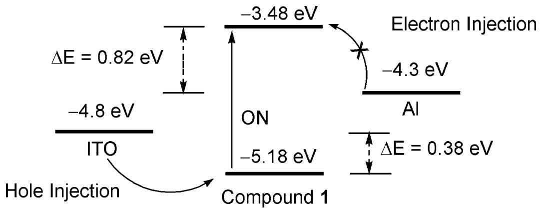

Figure 4. Diagram of the charge injection process in the **1**-based memory devices.

In conclusion, a novel small-molecule boron(III)-containing donor–acceptor compound with goldlike reflective behavior has been synthesized and employed in the fabrication of electronic resistive memory devices. The thin films prepared from **1** are found to exhibit goldlike reflective behavior with the percentage reflectance of the film found to be as high as 37% and the reflective region covering from $\lambda = 450$ to 1300 nm, which is suggestive of its potential application as optical reflector. Good memory device performances have been demonstrated with low threshold voltages of 2.8–3.4 V, high ON/OFF ratios of up to 10^7, low reading potentials of 1 V, and long retention times of over 10^4 s. By utilizing the present molecular design strategies, it is envisaged that different types of memory devices with tunable performance can be achieved. Further investigations on the understanding of the structure–activity relationships by the introduction of different donor groups into boron(III) diketonates as well as the mechanistic studies on the goldlike reflective behavior and memory effect are now in progress.

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Keywords: boron · donor-acceptor systems · optical reflector · molecular devices · thin films

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