Macromolecules

Synthesis, Characterization, Charge Transport, and Photovoltaic Properties of Dithienobenzoquinoxaline- and Dithienobenzopyridopyrazine-Based Conjugated Polymers

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ABSTRACT: Two donor-acceptor polymers (P1 and P2) based on dithienobenzoquinoxaline (M1) and dithienobenzopyridopyrazine (M2) as acceptor and indacenodithiophene as donor were synthesized via Stille polycondensation. The fused dithienobenzene unit in M1 and M2 units can improve the intermolecular stacking of polymer and also decrease the steric hindrance. P1, with dithienobenzoquinoxaline acceptor, shows a band gap of 1.61 eV. The band gap of P2 was reduced to 1.48 eV after changing to dithienobenzopyridopyrazine as the acceptor unit. The mobilities of P1 and P2 reach 5.6×10^{-2} and 1.5×10^{-2} cm² V⁻¹ s⁻¹, respectively. The results from photovoltaic measurements showed a very promising PCE of 6.06% for the P1/PC₇₁BM blend system without any thermal or solvent treatments, showing a great offer for the roll-to-roll manufacturing of PSCs.



INTRODUCTION

Polymer solar cells (PSCs) recently have been the subject of extensive investigations as a potential alternative energy source because of their light weight and potential for low-cost solution processing through roll-to-roll printing.¹ Bulk heterojunction (BHJ) photovoltaic cells containing the blend film of low band gap conjugated polymer and fullerene derivative like phenyl-C₆₁butyric acid methyl ester (PC₆₁BM or PC₇₁BM) as an active layer are the most commonly studied PSCs.^{1a,b,2} Recently, high power conversion efficiencies (PCEs) of more than 7% have been reported based on some conjugated polymer/PCBM blend systems, such as PTB7/PC71BM and PBDTTT-CF/PC71BM, etc.³ In general, the morphology of these blend systems is very sensitive to the processing conditions, which need be carefully tuned by the addition of high boiling point additives to the processing solvent. These processing conditions, however, are unfavorable for large area roll-to-roll manufacturing because of the possibility that these additives will remain as contaminants in the device following solvent evaporation.^{1c,4} Therefore, the rollto-roll printing process of PSCs will greatly benefit if a conjugated polymer/PCBM blend system could show high performance without using solvent additives and/or solvent/thermal annealing.

Alternating donor–acceptor (D–A) conjugated polymers have recently received more and more attention as a viable method to develop low band gap polymers because of their easily tunable band gap, energy levels, and charge mobility.^{1a,b,2a,2b,5} Among the acceptors, the electron-deficient quinoxaline unit is a quite promising one.⁶ Figure 1 shows some reported quinoxaline-based polymers. It can be seen that most of them have a thiophene spacer between donor (such as fluorene, carbazole) and quinoxaline units with the aim of lowering the band gap in resulting polymers. However, most of these polymers still possess relatively large band gaps of more than 1.90 eV, which partially limits the further development of quinoxaline-based polymers.^{6c} As seen from the chemical structure of quinoxaline unit (Figure 1), one can find that there are two ways to further modify the quinoxaline unit which can lead to changes in band gaps and energy levels of such polymers. One is from the top pyrazine unit, in which different substitutes (such as hydrogen, methyl, and phenyl) could be introduced to affect the band gaps of resulting polymers.^{6a-d} Another method is to change the benzene unit in the bottom of quinoxaline unit to more electron-deficient moiety (such as pyridine), which could significantly change the band gaps and energy levels of resulting polymers.

Herein, we present two alternating D–A polymers (P1 and P2) based on dithienobenzoquinoxaline (M1) and dithienobenzopyridopyrazine (M2) (Scheme 1) as the electron-deficient acceptor and an indenodithiophene (IDT) as the electron-rich donor. As seen from Scheme 1, M1 and M2 possess a large fused benzodithiophene ring on top of pyrazine unit, which is different from most quinoxaline units found in the literature (Figure 1). The large fused ring presents some advantages over other quinoxaline units. First of all, the fused dithiophene ring could decrease the steric hindrance compared to the freely rotating dithiophene unit and also form a planar structure to improve the intermolecular stacking of polymers as we have demonstrated in our previous report.⁷ Further, the extended π -conjugation in the fused qunioxaline unit will act as a strong electron-deficient acceptor, thus resulting a lower band gap in P1 and P2.⁷ In

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Figure 1. Chemical structures of several reported quinoxaline-based polymers.

Scheme 1. Synthesis of Monomers M1 and M2



addition, M2 contains a more electron-deficient pyridine unit in the bottom that could lead to a smaller band gap of P2 compared to P1. To this end, polymers P1 and P2 were synthesized via Stille polycondensation, and their optical, electrochemical, fieldeffect transistor, and photovoltaic properties were investigated.

RESULTS AND DISCUSSION

Synthesis. The synthetic route of monomers **M1** and **M2** is shown in Scheme 1. Previously, the benzo[2,1-b:3,4-b'] dithiophene-4,5-dione (3) was commonly synthesized from 2,2'-bithiophene-3,3'-dicarboxaldehyde through the oxidation with NaCN or KCN.⁸ To avoid using the highly toxic compound, an alternative method was used. As shown in Scheme 1, it involves lithiation of 3,3'-dibromo-5,5'-bis(trimethylsilyl)-2,2'-bithiophene (1) following by quenching using 1,4-dimethyl-2,3-piper-azinedione to give 2,7-trimethylsilylbenzo[2,1-b:3,4-b'] dithiophene-4,5-dione (2) in 57% yield. After removing the trimethylsilyl protective group using trifluoroacetic acid in dichloromethane, compound **3** was obtained in a total yield of 51% starting from compound **1**. The monomers **M1** and **M2** were then synthesized from the condensation of compound **3** with 3,6-dibromo-1,2-

benzenediamine (4) and 2,5-dibromo-3,4-pyridinediamine (5), respectively, in ethanol/acetic acid or ethanol. The corresponding yellow precipitate was recrystallized from chloroform to give the pure monomers **M1** and **M2** in the yield of 85% and 35%, respectively. The low yield of monomer **M2** is due to the low reactivity of compound 5. Compound 6 was synthesized by a modified method based on previous reports.^{7,9}

Scheme 2 shows the synthetic route of the polymers. Under the Stille coupling conditions, the polymers (P1 and P2) were synthesized from the reaction of monomers M1 and M2 with the bis-stannyl compound 6 using toluene as the solvent and Pd₂-(dba)₃ and P(*o*-tol)₃ as the catalyst. The polymers were purified by Soxhlet extraction with acetone and hexane to remove small molecular and residual catalyst. The polymers P1 and P2 show moderate solubility in chloroform (less than ~2 mg/mL), but good solubility in chlorobenzene and *o*-dichlorobenzene (*o*-DCB). GPC was used to determine the molecular weights of the polymers. The number-average molecular weight (M_n) of P1 and P2 is 21.0 and 16.0 kDa, respectively, with the polydispersity index (PDI) of 2.85 and 2.20 and the repeat unit of ~15, respectively.

Scheme 2. Synthetic Route toward Polymers P1 and P2





Figure 2. UV-vis absorption spectra of P1 and P2 in chloroform and thin films.

Optical and Electrochemical Properties. The optical properties of **P1** and **P2** were investigated in their chloroform solutions and thin films. Figure 2 shows the absorption spectra of **P1** and **P2** in chloroform and thin films. In chloroform solution, it can be seen that **P1** shows two main peaks: the high-energy peak with an absorption maximum at 445 nm comes from the donor part, and the low-energy peak with a maximum of 663 nm is due to the charge transfer from donor to acceptor. However, the polymer **P2** in chloroform solution shows a significant red-shift on the charge transfer peak with an absorption maximum at 721 nm, while the high-energy peak keeps almost same with that of **P1** because the same donor is used in both polymers. It shows that changing to the more electron-deficient pyridine unit in **P2** has a large effect on the optical property in comparison with that of **P1**. The optical band gap in solution for **P1** was determined to be 1.63 eV (760 nm). The



Figure 3. CV curves of P1 and P2 films.

optical band gap of P2 in solution is decreased to 1.51 eV (820 nm) due to the more electron-deficient pyridine in polymer backbone. It is interesting that the UV-vis spectra of P1 and P2 in thin films (Figure 2) exhibit similar features with that in solution. The charge transfer peak for P1 and P2 in thin film is at 651 and 720 nm, respectively. These results suggest that the polymers in solution likely already show a certain degree of packing, which is similar to what is observed in thin film. Further, the fused ring unit also promotes stronger chain stacking in solution and thin film compared with those polymers with free-rotated aromatic rings in quinoxaline unit, in which a significant blue-shift in thin film absorption is observed compared with that in solution.⁷ The absorption onsets of P1 and P2 are ~770 and ~835 nm, respectively, corresponding to an optical band gap of 1.61 and 1.48 eV, respectively. This value is around 0.3-0.6 eV smaller than other quinoxaline-based polymers (Figure 1).^{6a-d}



Figure 4. Output at different gate voltage (V_{gs}) (a, P1; c, P2) and transfer characteristics (b, P1; d, P2) in the saturation regime under constant sourcedrain voltage ($V_{ds} = -100 \text{ V}$) for FET devices.

Cyclic voltammetry (CV) was used to determine the HOMO and LUMO energy levels of P1 and P2 with a Pt counter electrode and a Ag/Ag⁺ reference electrode in 0.1 M tetrabutylammonium hexfluorophosphate in acetonitrile at a scan rate of 100 mV s⁻¹. The polymer thin films were coated on ITO from chlorobenzene solutions. The HOMO and LUMO energy levels were calculated from the literature method.^{5d,e} Figure 3 shows the CV curves of P1 and P2 thin films. It can be seen that both polymers exhibited good reversible oxidations and reduction peaks, except for the partially reversible reduction in P1. The HOMO energy levels of P1 and P2 were calculated to be -5.23and -5.26 eV, respectively, with ferrocene as reference. The LUMO energy levels of P1 and P2 are -3.53 and -3.69 eV, respectively, as calculated from the CV curves. It is well-known that the HOMO energy level is mainly determined by the donor part. Therefore, P1 and P2 show the similar HOMO energy levels because the same donor moiety is used. In contrast, the LUMO energy level is mainly delocalized on the acceptor part. Thus, a lower LUMO energy level (-3.69 eV) was found in P2 compared with P1 due to the more electron-deficient characteristic of pyridine unit in P2. Accordingly, it can be concluded that the reduced band gap of P2 compared to P1 is mainly caused by the lower LUMO energy level of P2. Similar phenomena were also found in other pyridine-based acceptors.¹⁰ The band gaps of **P1** and **P2**, as determined from CV, are 1.70 and 1.57 eV, respectively, which is in line with the measured optical band gap.

Field-Effect Transistor Properties. Charge carrier mobility is important to the performance of BHJ PSCs. Here, the top contact organic field-effect transistors (OFETs) coated with the polymers were fabricated to determine the field-effect mobility (μ) . The detailed fabrication procedure was reported in the literature.¹¹ Because of the limited solubility of both polymers in chloroform and strong dewetting of hexamethyldisilazane (HDMS) surface from o-dichlorobenzene solution, P1 was spun-cast from its chlorobenzene solution and P2 film was deposited from the mixture of chloroform and o-dichlorobenzene (1:1). Figure 4 shows the output at different gate voltage (V_{gs}) and transfer characteristics under constant source-drain voltage ($V_{ds} = -100 \text{ V}$) of **P1** and **P2** devices. The hole mobility of pristine P1 and P2 films determined from the saturation regime were 5.6×10^{-2} and 1.50×10^{-2} cm² V⁻¹ s⁻¹ with an on-off ratio of $\sim 10^3 - 10^5$, respectively. It is noted that the values were achieved from the polymer films without any thermal annealing. Further annealing leads to little change on the hole mobility presumably because the polymer chains already have quite strong packing.

Photovoltaic Properties. The photovoltaic properties of the polymers were investigated with a conventional



Figure 5. J-V curves (a) of P1/PC₇₁BM and P2/PC₇₁BM (1:3 wt) and EQE curves (b) of the conventional devices.



Figure 6. AFM figures of P1:PC₇₁BM (1:3, w/w) (a) and P2:PC₇₁BM (1:3, w/w) (b) blend films. The size of the AFM images is 5 μ m × 5 μ m.

device configuration of ITO/PEDOT:PSS/polymer:PC71-BM (1:3)/Ca/Al. Device performance was measured under 100 mW/cm^2 AM 1.5 illumination. The active layers were spin-coated from o-DCB solutions of polymer and PC₇₁BM. The optimized weight ratio between the polymer and PC71BM is 1:3. PC71BM was used as the electron acceptor due to the complementary absorption to the polymer in the visible region.¹² Figure 5a shows the J-V curves of the best P1 and P2 devices. The P1 device shows a V_{oc} of 0.83 V, a short-circuit current density (J_{sc}) of 11.6 mA cm⁻², and a fill factor (FF) of 0.63, resulting a high PCE of 6.06%. It is noted that such a high PCE is achieved without any pre- and/or post-treatments, such as thermal annealing, solvent/vapor annealing, or the addition of solvent additives. This is one of the highest PCE reported so far in BHJ PSCs without any thermal or solvent treatments.

Under the same conditions, the P2 device only showed a PCE to 3.21% with a V_{oc} of 0.74 V, a J_{sc} of 10.1 mA cm⁻², and a FF of 0.43. The low performance in the P2 device is well below what is expected because P2 possesses a lower HOMO energy level potential leading to a higher V_{oc} and lower band gap which favors a high J_{sc} . Although it is well-known that the V_{oc} is dependent on the difference between HOMO energy level of the donor and LUMO energy level of the acceptor,¹³ there are still some more factors affecting the V_{oc} such as the cathode, interface resistance,

and excition nonradiative recombination.¹⁴ In this case, it is most likely that excition nonradiative recombination at the interface is one of the reasons for the lower V_{oc} and J_{sc} since the pyridine unit may play a role as an electron trap compared with benzene unit in **P1**.¹⁰ In addition, the lower LUMO level of **P2** will also potential have a negative effect on charge separation, thereby resulting in a lower J_{sc} and reducing PCE even further. Having said that, it is interesting that **P2** devices are still able to show a J_{sc} of as high as 10 mA cm⁻².

To evaluate the accuracy of measurement, the external quantum efficiencies (EQEs) of both devices were measured. The EQE curves of P1 and P2 devices are shown in Figure 5b. The P1 device shows an efficient photoresponse from 350 to 750 nm, and the photoresponse of P2 device extended to around 800 nm as a result of red-shift absorption compared with P1. The EQE value of P1 device shows more than 40% between 350 and 700 nm with the highest value of 65% at \sim 400 nm. It is noted that the EQE shows a flat decrease from over 60% at short wavelengths to \sim 40% at 680 nm, indicating the balanced contribution from the shorter and longer wavelength absorption of P1 and $PC_{71}BM$. However, in P2 device, there is a significant decrease on EQE value from \sim 65% to 15% between 350 and 800 nm, and the main contribution to the EQE is from $PC_{71}BM$ and the short wavelength absorption of P2. The result is consistent with the lower J_{sc} in P2 device than that in P1 device. The calculated J_{sc} values in P1 and P2 devices are 11.8 and 9.47 mA cm⁻², respectively, which are in line with those values measured under AM 1.5G illumination.

The morphology of the polymer and PC71BM blend films was investigated by tapping-mode atomic force microscopy (AFM). Figure 6 shows the AFM figures of P1:PC₇₁BM (1:3, w/w) and **P2**:PC₇₁BM (1:3, w/w) films. Both films show a very smooth surface and small degree of phase separation, which should facilitate charge separation and potentially lead to high performance. The root-mean-square roughness is 0.964 and 0.845 nm for P1 and P2 blend films, respectively. It is known that an interpenetrating bicontinuous network between polymer and PCBM with an ideal domain size of 10–20 nm is important for high-performance PSCs. Both larger and smaller domain sizes of the blend films are not favorable for efficient charge transfer and separation. In addition, better miscibility and smaller domain sizes between polymer and PCBM should increase the possibility for charge recombination. The smaller roughness and better miscibility of P2 and PC₇₁BM compared to the P1 blend film could lead to charge recombination, and thus it may be a cause of the low *I*_{sc} in **P2**-based device relative to **P1**-based device. Further detailed studies on the charge transfer and excition separation and recombination are in progress and will be reported elsewhere.

CONCLUSION

Copolymers of indacenodithiophene and dithienobenzoquinoxaline, P1 and P2, have been designed and synthesized via Stille polycondensation. The fused benzodithiophene in dithienobenzoquinoxaline improves the intermolecular stacking of polymers and decreases the steric hindrance. The extended π -conjugation in the fused system also contributes to the low band gaps of P1 and P2. In addition, changing the benzene ring in the bottom of dithienobenzoquinoxaline to a more electron-deficient pyridine ring gives a further decrease in the band gap of P2 compared with that of P1. The HOMO and LUMO levels measured from CVs are -5.23 and -3.53 eV for P1 and -5.26 and -3.69 eV for P2, respectively. Furthermore, encouraging hole mobilities of as high as 5.6×10^{-2} and 1.5×10^{-2} cm² V⁻¹ s⁻¹ for P1 and P2 were achieved. Finally, the photovoltaic properties were investigated with the device structure of ITO/PEDOT: PSS/polymer:PC71BM (1:3, w/w)/Ca/Al. A PCE of 6.06% with a $V_{\rm oc}$ of 0.83 V, a $J_{\rm sc}$ of 11.6 mA cm⁻², and a FF of 0.63 for a P1based device was achieved without any thermal or solvent treatments. We believe that P1 will be one of the very promising candidates for offering roll-to-roll manufacturing of PSCs.

EXPERIMENTAL SECTION

Materials and General Characterization Method. All reagents were purchased from commercial sources without further purification. 3,3'-Dibromo-5,5'-bis(trimethylsilyl)-2,2'-bithiophene (1), 3,6-dibromo-1,2-diaminobenzene (4), 2,5-dibromo-3,4-diaminopyridine (5), and compound 6 were prepared by following literature procedures.^{7,9,10} UV–vis spectra were obtained using a Perkin-Elmer Lambda-9 spectrophotometer. The ¹H NMR spectra were collected on a Bruker AV 300 or 500 spectrometer operating at 300 MHz in deuterated chloroform solution with TMS as reference. Cyclic voltammetries of polymer films were conducted in acetonitrile with 0.1 M of tetrabuty-lammonium hexafluorophosphate using a scan rate of 100 mV s⁻¹. ITO, Ag/AgCl, and Pt mesh were used as working electrode, reference electrode, and counter electrode, respectively. The molecular weight and polydispersity were analyzed by a Waters 1515 gel permeation

chromatograph (GPC) with a refractive index detector at 35 $^{\circ}$ C (THF as the eluent). AFM images under tapping mode were taken on a Veeco multimode AFM with a Nanoscope III controller.

Device Fabrication and Characterization. The FET devices were fabricated following the procedure of our previous report.⁵ The polymer solar cells were fabrication as following: ITO-coated glass substrates (15 Ω/sq) were cleaned with detergent, deionized water, acetone, and isopropyl alcohol. A thin layer (ca. 40 nm) of PEDOT:PSS (Baytron P VP AI 4083, filtered at 0.45 μ m) was first spin-coated on the precleaned ITO-coated glass substrates at 5000 rpm and baked at 140 °C for 10 min under ambient conditions. The substrates were then transferred into an argon-filled glovebox. Subsequently, the polymer: PC71BM active layer (ca. 90 nm) was spin-coated on the PEDOT:PSS layer from a homogeneously blended solution. The solution was prepared by dissolving the polymer at a blend weight ratio of 1:3 in o-dichlorobenzene and filtered with a 0.2 μ m PTFE filter. At the final stage, the substrates were pumped down to high vacuum ($< 2 \times 10^{-6}$ Torr), and calcium (30 nm) topped with aluminum (100 nm) was thermally evaporated onto the active layer through shadow masks to define the active area of the devices. The unencapsulated solar cells were tested under ambient conditions using a Keithley 2400 SMU and an Oriel xenon lamp (450 W) with an AM1.5 filter. A mask was used to define the device illumination area of 10.08 mm² to minimize photocurrent generation from the edge of the electrodes. The light intensity was calibrated to 100 mW/cm² using a calibrated silicon solar cell with a KG5 filter, which has been previously standardized as the National Renewable Energy Laboratory.

Synthesis. *Compound* **2**. To a solution of compound 1 (3.15 g, 6.7 mmol) in THF (30 mL) was added *n*-BuLi (6.5 mL, 2.5 M in hexane) at -78 °C. The resulting mixture was kept at -78 °C for 1 h. 1,4-Dimethyl-2,3-piperazinedione (1.2 g, 8.5 mmol) was added in one portion, and then the mixture was stirred at room temperature for 1 h. 1 M HCl (50 mL) was added into the mixture. The mixture was extracted with dichloromethane. The dichloromethane layer was washed with water and dried over anhydrous Na₂SO₄. After removing the solvent under vacuum, a black solid was achieved after purifying through column with dichloromethane as eluent (1.4 g, 57%). ¹H NMR (300 MHz, CDCl₃, δ): 7.63 (s, 2H), 0.39 (s, 18H). ¹³C NMR (125 MHz, CDCl₃, δ): 175.48, 148.60, 142.72, 136.10, 134.61, -0.20. GC-MS (*m/z*): calcd for C₁₆H₂₀O₂S₂Si₂, 364.04; found, 364.

Compound **3**. Compound **2** (1.5 g, 4.1 mmol) was dissolved into dichloromethane (20 mL), and TFA (6 mL) was added. The mixture was stirred at room temperature for 1 h and then refluxed for overnight. After TLC monitor showed completed reaction, the mixture was cooled to room temperature. After removing the solvent, the crude product was purified by silica column to give a black solid in 89% yield. ¹H NMR (300 MHz, CDCl₃, δ): 7.52 (d, *J* = 5.22 Hz, 2H), 7.24 (d, *J* = 5.22 Hz, 2H). ¹³C NMR (125 MHz, CDCl₃, δ): 174.84, 144.15, 135.36, 128.09, 125.82. GC-MS (*m*/*z*): calcd for C₁₀H₄O₂S₂, 219.96; found, 219.

Compound **M1**. To a 50 mL flask charged with compounds **3** and **4** was added ethanol (30 mL) and acetic acid (10 mL). Following heating at refluxed for 2 days, a yellow precipitation was collected by filtration and washed with cold ethanol. Further purification through recrystallization in chloroform gave the yellow compound in the yield of 85%. ¹H NMR (300 MHz, CDCl₃, δ) 8.58 (d, *J* = 3.12 Hz, 2H), 8.09 (s, 2H), 7.67 (d, *J* = 3.18 Hz, 2H). HRMS (ESI) (M⁺, C₁₆H₆Br₂N₂S₂): calcd, 447.8339; found, 440.8332.

Compound **M2**. The compound **M2** was synthesized by following the method of **M1**; however, pure ethanol was used as the solvent. ¹H NMR (300 MHz, CDCl₃, δ): 8.89 (s, 1H), 8.58 (m, 2H), 7.72–7.69 (dd, 2H). HRMS (ESI) (M⁺, C₁₅H₅Br₂N₃S₂): calcd, 448.8292; found, 448.8286.

Synthesis of **P1**. Monomer 6 (265 mg, 0.21 mmol) and **M1** (90 mg, 0.20 mmol) were charged into a 25 mL flask fitted with a condenser under N₂ protection. Dry toluene (4 mL) was added into the flask followed by adding Pd₂(dba)₃ (9 mg) and P(*o*-tol)₃ (23 mg). The resulting mixture was then degassed twice and heated up to ~120 °C for 3 days. After cooling to room temperature, the mixture was poured into methanol. The precipitate was then purified by Soxhlet extraction with acetone and hexane for 12 h. The collected solid was then dissolved into a small amount of chlorobenzene, which was then precipitated into acetone. Last, the black solid was collected and dried overnight under vacuum (198 mg, 83%). ¹H NMR (300 MHz, CDCl₃, δ) 8.59–8.08 (br, 4H), 7.79–7.09 (br, 22H), 2.64 (br, 8H), 1.66–1.53 (m, 8H), 1.29 (m, 24H), 0.88 (m, 12H).

Synthesis of **P2**. **P2** was synthesized with monomer **6** (262 mg, 0.21 mmol) and **M2** (89 mg, 0.20 mmol) by following a similar procedure to that of **P1** (210 mg, 88%). ¹H NMR (500 MHz, CDCl₃, δ): 9.18–8.13 (br, 3H), 7.82–7.09 (br, 22H), 2.64 (br, 8H), 1.66–1.53 (m, 8H), 1.29 (m, 24H), 0.88 (m, 12H).

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