D-A-D structured organic molecules with diketopyrrolopyrrole acceptor unit for solution-processed organic solar cells

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Four solution-processable D-A-D structured organic molecules with diketopyrrolopyrrole (DPP) as acceptor unit and triphenylamine (TPA) or (4-hexyl) thiieno [3,2-b]thiophene (HTT) as donor unit, DPP8-TPA, DPP8-TPA-OR, DPP6-HTT and DPP8-HTT, were designed and synthesized for the application as donor materials in solution-processed organic solar cells (OSCs). The molecules show broad absorption and relatively lower highest occupied molecular orbital energy levels. Photovoltaic properties of the molecules were investigated by fabricating the bulk-heterojunction OSCs with the molecules as donor and PC71BM as acceptor. Power conversion efficiency of the OSC based on DPP8-HTT reached 1.5% under the illumination of AM1.5, 100 mW cm\(^{-2}\).

1. Introduction

Solution-processable organic small molecules have attracted much interest recently for applications in organic solar cells (OSCs) [1–10] owing to their advantages of high purity and definite molecular weight in comparison with conjugated polymers, and the low-cost solution processability in comparison with vaccum-deposited small molecule photovoltaic materials. In the molecular design of photovoltaic donor materials in solution-processed OSCs, good solubility, narrower band gap with broad absorption, relatively lower HOMO (the highest occupied molecular orbital) energy level and higher hole mobility are...

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key issues for high photovoltaic performance \[11\]. Among the requisites of the properties, good solubility of the organic donor materials is required for solution-processing. Broad absorption, relatively lower HOMO level and higher hole mobility of the donor materials are needed for greater short circuit current \(J_{sc}\), higher open-circuit voltage \(V_{oc}\) and larger fill factor (FF) to get higher power conversion efficiency (PCE) of the OSCs.

Roncali and colleagues were the first to use triphenylamine (TPA)-containing molecules in the solution-processed OSCs \[12–14\]. Benefitting from the three-dimensional propeller structure and good hole-transporting property of TPA units, TPA-containing molecules show good solubility and attractive photovoltaic performance \[12–23\]. The highest PCE of the solution-processed OSCs based on a star-shaped TPA-containing molecule as donor and PC71BM as acceptor reached 4.3\% \[20\]. Nguyen and colleagues introduced diketopyrrolopyrrole (DPP) unit into the solution-processable organic molecule photovoltaic materials \[24–26\]. A linear D-A-D structured molecule DPP(TBFu)\(_2\) with DPP as acceptor (A) unit, benzo furan as donor (D) unit and thiophene as pi-bridges, possesses a broad absorption and suitable electronic energy levels. The solution-processed OSCs based on DPP(TBFu)\(_2\) as donor and PC71BM as acceptor demonstrated a PCE of 4.4\% \[25\].

Here, we designed and synthesized a series of new linear and D-A-D structured molecule donor materials, DPP8-TPA, DPP8-TPA-OR, DPP6-(4-hexyl)thieno\[3,2-b\]thiophene (HTT) and DPP8-HTT, with DPP as core and acceptor unit, TPA or thieno\[3,2-b\]thiophene (TT) as donor unit with different substituents for modulating the solubility, absorption spectra, HOMO energy levels and hole mobility of the molecules. The TPA unit used in the molecules is for good solubility and higher hole mobility as mentioned above \[12–23\]. The consideration of using the TT unit in DPP8-HTT and DPP6-HTT is from the planar structure and higher hole mobility of the molecules containing the fused thiophene unit \[27–29\]. The four molecule films of DPP8-TPA, DPP8-TPA-OR, DPP6-HTT and DPP8-HTT show good thermal stability and broad absorption band in the range 350–750 nm. The solution-processed OSCs based on the blend of DPP8-HTT and PC71BM (1 : 3, w/w) reached 1.50\% under the illumination of AM1.5G, 100 mW cm\(^{-2}\).

2. Results and discussion

(a) Synthesis and thermal properties

The four linear molecules were synthesized by the palladium-catalysed Heck and Suzuki reaction, as shown in Scheme 1. Monomers 1–5 were synthesized according to the literature \[24,27,30\]. The four compounds are soluble in common organic solvents, such as CHCl\(_3\), tetrahydrofuran (THF), chlorobenzene and toluene.

The thermal stability of the compounds was investigated by thermogravimetric analysis (TGA). The temperatures with 5\% weight loss are at 368°C, 363°C, 366°C and 337°C for DPP8-TPA, DPP8-TPA-OR, DPP6-HTT and DPP8-HTT, respectively, as shown in figure 1. The stability of the materials is good enough for application in optoelectronic devices.

(b) Absorption spectra

Figure 2 shows the UV-vis absorption spectra of the four compounds in chloroform solutions and in solid films. The optical absorption peak wavelength (\(\lambda\)) of the compounds is summarized in table 1. Benefitting from their D-A molecular structure, the absorption spectra of the four compound solutions in chloroform exhibit an absorption peak at around 350 nm and a strong absorption band in the wavelength range from 400 to 700–750 nm, as shown in figure 2a. The strong absorption band in the visible region could be assigned to the intramolecular charge transfer transition between the donor moiety (TPA, TT) and DPP acceptor unit. Owing to the stronger electron donating effects of the TPA unit, DPP8-TPA and DPP8-TPA-OR solutions exhibit more red-shifted absorption (by ca 30 nm) than that of DPP6-HTT and DPP8-HTT solutions.
Scheme 1. Synthetic routes of DPP8-TPA, DPP8-TPA-OR, DPP6-HTT and DPP8-HTT. I Pd(OAc)$_2$, NaOAc, $n$-Bu$_4$NBr, DMF, 100°C for 24 h, under N$_2$; II Pd$_2$ (dba)$_3$, K$_3$PO$_4$ (2 mol l$^{-1}$), toluene, 120°C reflux for 24 h.

Figure 1. TGA plots of DPP8-TPA, DPP8-TPA-OR, DPP6-HTT and DPP8-HTT.

For all four molecules, the absorption peaks of their films (figure 2b) red shifted in comparison with their dilute solutions, and the red shift of the DPP6-HTT and DPP8-HTT films is much greater than that of DPP8-TPA and DPP8-TPA-OR films, indicating that there is stronger intermolecular interaction in the TT-containing compound films than that of the TPA-containing compound films. Obviously, better planarity of the TT-containing molecules benefits the stronger intermolecular interaction. Moreover, the absorption spectrum of DPP8-TPA and DPP6-HTT films
1.0 DPP8-TPA solution
DPP8-TPA film
DPP8-TPA-OR film
DPP6-HTT film
DPP8-HTT film
DPP8-TPA-OR solution
DPP6-HTT solution
DPP8-HTT solution

Figure 2. (a,b) UV-vis absorption spectra of DPP8-TPA, DPP8-TPA-OR, DPP6-HTT and DPP8-HTT in chloroform solution and film state. (Online version in colour.)

Table 1. Absorption spectra and electrochemical properties of compounds DPP8-TPA, DPP8-TPA-OR, DPP6-HTT and DPP8-HTT.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>λ_{solution} (nm)</th>
<th>λ_{film} (nm)</th>
<th>$E_{\text{red onset}}$ (V)/LUMO (eV)</th>
<th>$E_{\text{ox onset}}$ (V)/HOMO (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DPP8-TPA</td>
<td>370/626/664</td>
<td>379/640/693</td>
<td>-1.19/3.52</td>
<td>0.43/-5.14</td>
</tr>
<tr>
<td>DPP8-TPA-OR</td>
<td>371/639/676</td>
<td>376/641/703</td>
<td>-1.18/3.53</td>
<td>0.32/-5.03</td>
</tr>
<tr>
<td>DPP6-HTT</td>
<td>364/595/636</td>
<td>392/641/716</td>
<td>-1.13/3.58</td>
<td>0.55/-5.26</td>
</tr>
<tr>
<td>DPP8-HTT</td>
<td>364/598/634</td>
<td>379/609/685</td>
<td>-1.18/3.53</td>
<td>0.47/-5.18</td>
</tr>
</tbody>
</table>

is more red shifted than that of DPP8-TPA-OR and DPP8-HTT films, respectively, indicating that fewer or shorter side chains in the molecules result in stronger intermolecular interactions.

(c) Electrochemical properties

Electrochemical cyclic voltammetry was carried out for measuring the HOMO and LUMO energy levels of the compounds. Figure 3 shows the cyclic voltammograms of DPP8-TPA, DPP8-TPA-OR, DPP6-HTT and DPP8-HTT films and the values of the onset reduction potentials ($E_{\text{red onset}}$); onset oxidation potentials ($E_{\text{ox onset}}$) of the compounds are listed in Table 1. It can be seen from figure 3
Figure 3. Cyclic voltammograms of DPP8-TPA, DPP8-TPA-OR, DPP6-HTT and DPP8-HTT films on Pt electrode in an acetonitrile solution of 0.1 mol l\(^{-1}\) Bu\(_4\)NPF\(_6\) (Bu = butyl) with a scan rate of 100 mV s\(^{-1}\). That the oxidation processes of the two HTT-based molecules DPP6-HTT and DPP8-HTT are reversible, but the reduction processes of the four compounds are irreversible.

The HOMO, LUMO energy levels and the electrochemical band gaps of the four materials were estimated, respectively, from the onset oxidation and reduction potentials according to the following equations [31,32]:

\[
E_{\text{HOMO}} = -e(E_{\text{ox onset}} + 4.71) \text{(eV)}, \quad E_{\text{LUMO}} = -e(E_{\text{red onset}} + 4.71) \text{(eV)},
\]

and

\[
E_{\text{g}} = E_{\text{LUMO}} - E_{\text{HOMO}}.
\]

The LUMO energy levels of the four compounds are around \(-3.5\) eV, which change little for different molecules. But the HOMO energy levels of the molecules change greatly from \(-5.03\) eV for DPP8-TPA-OR to \(-5.26\) eV for DPP6-HTT (table 1). The molecules of DPP8-HTT and DPP6-HTT containing the TT unit show lower HOMO energy levels, which is beneficial to higher \(V_{\text{oc}}\) of the OSCs with the compounds as donor. The electrochemical band gaps of DPP8-TPA, DPP8-TPA-OR, DPP6-HTT and DPP8-HTT are 1.61, 1.50, 1.68 and 1.65 eV, respectively. Compared with the HOMO \((-5.87\) eV) and LUMO \((-3.91\) eV) energy levels for PC\(_{71}\)BM, [33] the compounds are suitable to be used as photovoltaic donors with PC\(_{71}\)BM as acceptor on the energy level point of view.

(d) Morphology of the blend films

The morphology of the photoactive layers is very important for the photovoltaic performance of OSCs [34]. We used atomic force microscopy (AFM) to investigate the morphology of the four organic molecules: PC\(_{71}\)BM (1 : 3, w/w) blend films. All of the AFM images of the blend films exhibit typical amorphous morphology without any crystalline domains, as shown in figure 4. The blend films of DPP8-TPA/PC\(_{71}\)BM and DPP6-HTT/PC\(_{71}\)BM exhibit bigger aggregates, compared with that of DPP-8-TPA-OR/PC\(_{71}\)BM and DPP8-HTT/PC\(_{71}\)BM.

(e) Photovoltaic properties

Bulk-heterojunction OSCs were fabricated by using the four compounds as donor, PC\(_{71}\)BM [35] as acceptor and Al as the negative electrode. The device structure is ITO/PEDOT: PSS/photoactive layer/Al. The active layer is composed of a blend film of the organic molecule donor and PC\(_{71}\)BM acceptor with a weight ratio of 1 : 3. Figure 5 shows the current density–voltage curves of the OSCs in the dark and under the illumination of AM 1.5, 100 mW cm\(^{-2}\). The photovoltaic performance data of the OSCs, including \(V_{\text{oc}}, J_{\text{sc}}, \text{FF}\) and PCE values, are summarized in table 2 for a clear comparison. The best PCE of the device based on DPP8-HTT reached 1.50% with a higher \(V_{\text{oc}}\) of 0.73 V and a \(J_{\text{sc}}\) of 6.62 mA cm\(^{-2}\). In comparison to the photovoltaic performance of DPP8-TPA and DPP8-HTT, it can be seen that DPP8-HTT showed higher \(V_{\text{oc}}\) and higher \(J_{\text{sc}}\) values than...
Figure 4. AFM images of the blend films of organic molecules: PC$_{71}$BM (1:3, w/w), the organic molecules are (a) DPP8-TPA, (b) DPP8-TPA-OR, (c) DPP6-HTT and (d) DPP8-HTT. The scan size of the images is 5 $\times$ 5 $\mu$m. (Online version in colour.)

Table 2. Photovoltaic performance of ITO/PEDOT : PSS/organic molecules: PC$_{71}$BM (1:3, w/w)/Al negative electrode under the illumination of AM1.5, 100 mW cm$^{-2}$.

<table>
<thead>
<tr>
<th>organic molecule in the active layer</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DPP8-TPA</td>
<td>0.58</td>
<td>5.00</td>
<td>30.0</td>
<td>0.90</td>
</tr>
<tr>
<td>DPP8-TPA-OR</td>
<td>0.63</td>
<td>5.66</td>
<td>34.0</td>
<td>1.20</td>
</tr>
<tr>
<td>DPP6-HTT</td>
<td>0.73</td>
<td>4.36</td>
<td>28.3</td>
<td>0.90</td>
</tr>
<tr>
<td>DPP8-HTT</td>
<td>0.73</td>
<td>6.62</td>
<td>30.5</td>
<td>1.50</td>
</tr>
</tbody>
</table>

that of DPP8-TPA, which indicates that the planar structure of the TT unit is beneficial to the improved photovoltaic performance of the compounds. The poorer photovoltaic performance of the OSC based on DPP6-HTT could be owing to the lower solubility of DPP6-HTT with too short side chains.

In conclusion, a series of linear D-A-D molecules, DPP8-TPA, DPP8-TPA-OR, DPP6-HTT and DPP8-HTT with DPP as core and acceptor unit and TPA or TT as donor unit, was designed and synthesized for application as donor materials in solution-processed OSCs. The four compound films show broad absorption band and lower band gap. The donor unit of TPA or TT and the side chains of the molecules influence the photovoltaic performance of the compounds significantly. The OSC devices based on a blend of DPP8-HTT and PC$_{71}$BM (1:3, w/w) exhibited a PCE of 1.50% with a $V_{oc}$ of 0.73 V and a $J_{sc}$ of 6.62 mA cm$^{-2}$, under the illumination of AM1.5, 100 mW cm$^{-2}$. The results indicate that the planar donor unit of TT is better than the TPA unit in the D-A-D structured DPP-containing molecules photovoltaic materials.

3. Experimental section

(a) Chemicals

TPA, $n$-butyllithium (2.50 mol l$^{-1}$ in hexane), tetrabutylammonium bromide, sodium acetate, palladium acetate, Pd$_2$(dba)$_3$, K$_3$PO$_4$, toluene and DMF were obtained from Acros Organics. THF was dried over Na/benzophenoneketyl and freshly distilled prior to use. Monomers 1–5
Figure 5. (a–d) Current density–voltage characteristics of the OSC devices based on the blends of linear molecules/PC$_{71}$BM (1:3, w/w) with Al as the negative electrode in the dark and under the illumination of AM1.5, 100 mW cm$^{-2}$.

were synthesized according the literature [24,27,30]. Other chemicals were common commercial chemicals and were used as received.

(b) Measurements

Nuclear magnetic resonance (NMR) spectra were taken on a Bruker DMX-400 spectrometer. MALDI-TOF spectra were recorded on a Bruker BIFLEXIII. Absorption spectra were taken on a Hitachi U-3010 UV-vis spectrophotometer. The film on quartz used for UV measurements was prepared by spin-coating with 1% chloroform solution. The TGA measurement was performed on a Perkin-Elmer TGA-7 apparatus. The electrochemical cyclic voltammetry was carried out with a Zahner IM6e electrochemical workstation in a 0.1 mol l$^{-1}$ tetrabutylammonium hexafluorophosphate (Bu$_4$NPF$_6$) acetonitrile solution. A glassy carbon electrode coated with the sample film was used as the working electrode, a Pt wire and Ag/Ag$^+$ (0.01 M AgNO$_3$ in acetonitrile) were used as the counter and reference electrodes, respectively.

(c) Fabrication and characterization of organic solar cells

OSC were fabricated in the configuration of the traditional sandwich structure with an ITO positive electrode and a metal negative electrode. Patterned ITO glass with a sheet resistance of 30 Ω sq$^{-1}$ was purchased from CSG Holding Co., Ltd (China). The ITO glass was cleaned in an ultrasonic bath of acetone and isopropanol and treated by UVO (ultraviolet ozone cleaner, Jelight Company, USA). Then a thin layer (30 nm) of PEDOT: PSS (poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate)) (Baytron PVP A1 4083, Germany) was spin-coated on the ITO glass. Subsequently, the photosensitive layer was prepared by spin-coating the blend solution of linear materials and PC$_{71}$BM (1:3 w/w) on the top of the PEDOT:PSS layer (ca 30 nm thickness) and baked at 80°C for 30 min. The concentration of the solution was 10 mg ml$^{-1}$ in chlorobenzene. The
thickness of the photoactive layer was measured using an Ambios Technology XP-2 profilometer. Finally, an Al electrode (ca 120 nm) was vacuum-evaporated on the photoactive layer under a shadow mask in the vacuum of ca $10^{-4}$ Pa. The current–voltage ($I$–$V$) measurement of the devices was conducted on a computer-controlled Keithley 236 Source Measure Unit. A xenon lamp coupled with AM1.5 solar spectrum filters was used as light source, and the optical power at the sample was 100 mW cm$^{-2}$.

(d) Synthesis

**DPP8-TPA:** monomer 1 (0.682 g, 1 mmol), N,N-diphenyl-N-(4-vinylphenyl)amine (0.596 g, 2.2 mmol), palladium (II) acetate (5 mg), tetra-$n$-butylammonium bromide (103 mg, 0.32 mmol) and sodium acetate anhydrous (1.64 g, 20 mmol) were dissolved and kept in degassed $N,N$-dimethyl formamide (30 ml), under argon at 100$^\circ$C for 24 h. The mixture was poured into water (30 ml). The precipitate was filtered, washed with water and dissolved in dichloromethane, and dried over anhydrous sodium sulfate. After evaporation of the solvent, the residue was purified by column chromatography (petroleum/dichloromethane, 1:1). Yield: 656 mg (62%). $^1$H NMR (CDCl$_3$, 400 MHz, $\delta$/ppm): 7.7 (d, 2H), 7.3 (d, 2H), 7.05 (d, 4H), 7.01 (t, 8H), 6.99 (m, 8H), 6.59 (m, 8H), 6.46 (m, 8H), 6.41 (d, 4H), 4.05 (d, 4H), 2.10 (m, 2H), 1.39 (m, 20H), 0.93 (t, 6H). MALDI-TOF MS: 1063.66, calcd for C$_{70}$H$_{70}$N$_4$O$_2$S$_2$ 1063.56. Anal. Calcd for C$_{70}$H$_{70}$N$_4$O$_2$S$_2$: C, 79.09; H, 6.59; N, 5.27. Found: C, 77.99; H, 6.79; N, 5.05.

**DPP8-TPA-OR:** monomer 1 (0.682 g, 1 mmol), N,N-di($n$-octyloxyphenyl)-4-(vinylphenyl)amine (1.16 g, 2.2 mmol), palladium (II) acetate (5 mg), tetra-$n$-butylammonium bromide (103 mg, 0.32 mmol) and sodium acetate anhydrous (1.64 g, 20 mmol) were dissolved and kept in degassed $N,N$-dimethyl formamide (30 ml), under argon at 100$^\circ$C for 24 h. The mixture was poured into water (30 ml). The precipitate was filtered, washed with water and dissolved in dichloromethane, dried over anhydrous sodium sulfate. After the evaporation of the solvent, the residue was purified by column chromatography (petroleum/dichloromethane, 2:1). Yield: 320 mg (20%). $^1$H NMR (CDCl$_3$, 400 MHz, $\delta$/ppm): 8.91 (d, 2H), 7.3 (d, 4H), 7.15 (d, 2H), 7.09 (m, 10H), 7.00 (m, 2H), 5.88 (m, 12H), 4.10 (t, 4H), 3.05 (d, 4H), 2.10 (m, 2H), 1.74 (m, 4H), 1.33 (m, 42H), 0.90 (t, 12H). MALDI-TOF MS: 1575.9, calcd for C$_{102}$H$_{134}$N$_4$O$_6$S$_2$ 1576.31. Anal. Calcd for C$_{102}$H$_{134}$N$_4$O$_6$S$_2$: C, 77.76; H, 8.51; N, 3.55. Found: C, 77.68; H, 8.64; N, 3.52.

**DPP6-HTT:** In a three-necked, oven-dried 100 ml round-bottom flask, monomer 4 (0.626 g, 1 mmol) was mixed with 15 ml of anhydrous toluene and 10 ml of 2.0 M potassium phosphate and the resulting mixture was degassed for 10 min. Monomer 5 (0.77 g, 2.2 mmol), tris(dibenzylideneacetone)dipalladium(0) (14 mg, 0.0153 mmol) and tri-$n$-tert-butyolphosphonium tetrafluoroborate (18 mg, 0.0620 mmol) were then added to the mixture and then degassed again for 5 min. The reaction mixture was stirred and heated to 120$^\circ$C under argon overnight. The reaction mixture was allowed to cool down to room temperature, then was poured into 300 ml of methanol and stirred for 30 min. The precipitated solid was then collected by vacuum filtration and washed with several portions of distilled water, methanol, isopropanol and petroleum ether. The crude product was purified by flash chromatography using chloroform as eluent, and the solvent was removed in vacuum to obtain a pure product. Yield: 520 mg (57%). $^1$H NMR (CDCl$_3$, 400 MHz, $\delta$/ppm): 8.97 (d, 2H), 7.48 (s, 2H), 7.34 (d, 2H), 6.99 (s, 2H), 4.12 (t, 4H), 2.74 (t, 4H), 1.77 (m, 8H), 1.47 (m, 4H), 1.36 (m, 20H), 0.91 (t, 12H). MALDI-TOF MS: 912.3, calcd for C$_{50}$H$_{60}$N$_2$O$_2$S$_6$ 913.4. Anal. Calcd for C$_{50}$H$_{60}$N$_2$O$_2$S$_6$: C, 65.78; H, 6.57; N, 3.07. Found: C, 65.35; H, 6.64; N, 3.13.

**DPP8-HTT:** In a three-necked, oven-dried 100 ml round-bottom flask, monomer 1 (0.683 g, 1.00 mmol) was mixed with 15 ml of anhydrous toluene and 10 ml of 2.0 M potassium phosphate and the resulting mixture was degassed for 10 min. Monomer 5 (0.77 g, 2.20 mmol), tris(dibenzylideneacetone)dipalladium(0) (14 mg, 0.0153 mmol), and tri-$n$-tert-butyolphosphonium tetrafluoroborate (18 mg, 0.0620 mmol) were then added to the mixture and then degassed again for 5 min. The reaction mixture was stirred and heated to 120$^\circ$C under argon overnight. The reaction mixture was allowed to cool down to room temperature, and then it was poured away...
into 300 ml of methanol and stirred for 30 min. The precipitated solid was then collected by vacuum filtration and washed with several portions of distilled water, methanol, isopropanol and petroleum ether. The crude product was purified by flash chromatography using chloroform as eluent, and the solvent was removed in vacuum to obtain a pure product. Yield: 490 mg (51%).

$^1$H NMR (CDCl$_3$, 400 MHz, δ/ppm): 8.96 (d, 2H), 7.46 (s, 2H), 7.33 (d, 2H), 7.02 (s, 2H), 4.02 (t, 4H), 2.74 (t, 4H), 1.94 (t, 2H), 1.77 (m, 4H), 1.38 (m, 34H), 0.94 (m, 12H). MALDI-TOF MS: 968.4, calcd for C$_{54}$H$_{68}$N$_2$O$_2$S$_6$ 969.52. Anal. Calcd for C$_{54}$H$_{68}$N$_2$O$_2$S$_6$: C, 66.94; H, 7.02; N, 2.89. Found: C, 65.97; H, 7.13; N, 2.84.

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References


