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# Synthesis, optical, electrochemical, and thermal properties of conjugated α-fluorenyl oligothiophenes

Vinich Promarak,* Auradee Punkvuang, Duangratchaneegorn Meunmat,
Taweesak Sudyoadsuk, Sayant Saengsuwan and Tinnagon Keawin

*Advanced Organic Materials and Devices Laboratory, Department of Chemistry, Faculty of Science,
Ubon Ratchathani University, Warinchumrap, Ubon Ratchathani 34190, Thailand*

**Abstract**—A series of new α-fluorenyl oligothiophenes up to the pentamer have been synthesized using Suzuki cross-coupling and bromination reactions. The optical, electrochemical, and thermal properties of these materials can be tuned by varying the number of thiophene rings. The longer oligomers ($n \geqslant 4$) were stable, crystalline, and unreactive to electrochemical oxidative dimerization. © 2006 Elsevier Ltd. All rights reserved.

The study of well-defined oligomers has recently become useful to gain insight into structure–property relationships in order to rationalize the behavior of the corresponding polymers and also has provided information, which may be used to improve strategies for the development of novel organic materials.[1] The advantages of oligomers are that their physical properties can be easily tuned to the desired properties by changing the structure, for example, solubilizing chains, terminal groups, and different oligomer lengths. In particular, oligothiophenes had earlier been used as model compounds for polymers[2] and have been lately advanced as components for molecular electronic and optoelectronic devices.[3,4] To vary the structure and the properties of oligothiophenes, the introduction of different terminal groups into their backbone is at of increasing synthetic interest. For example, a series of oligothiophenes substituted at their terminal α,α′-positions with 2-n-hexyl-fluorene,[5] 9,9-diphenylfluorene,[6] diphenylamine,[7] cyclophane,[8] pyrene,[9] and bis(4-methylphenyl)amino-phenyl[4] have been synthesized and investigated recently. To our best knowledge, however, there are only a few reports on monosubtituted derivatives,[10–12] whose synthesis and physical properties still remain to be explored. In this Letter, we report a successful synthesis of a series of novel α-fluorenyl oligothiophenes up to the pentamer

with the aim of investigating the structure and physical property relationships of the materials.

The synthetic approach to a series of α-fluorenyl oligothiophenes is illustrated in Scheme 1. Due to the convenience and high yields, palladium-catalyzed Suzuki cross-coupling reactions[11] were employed to achieve growth of the oligothiophene segment. Bromine was selectively introduced to the α-position of the terminal thiophene ring by bromination with NBS to allow further Suzuki cross-coupling reactions to be performed. The fluorene compound **2** was synthesized in high yield by bis-alkylation at C-9 of 2-bromofluorene **1** with *n*-hexylbromide. Compound **FT1** was readily obtained via cross-coupling between **2** and 2-thiopheneboronic acid in the presence of Pd(PPh₃)₄ as a catalyst and 2 M Na₂CO₃ as a base in THF at reflux in 79% yield. Consequently, treatment of a **FT1** with NBS in THF afforded the intermediate bromo compound **3** in a good yield. Repetitive cross-coupling and bromination reaction sequences led to a series of α-substituted oligothiophenes up to the pentamers, **FT2**, **FT3**, **FT4**, and **FT5**, in good yields. Compounds **FTn** ($n = 1–5$) were fully characterized by $^1H$, $^{13}C$ NMR, IR, and HRMS analyses.[13] They exhibited a good solubility in organic solvents such as chlorinated solvents, THF, and acetone at room temperature.

The optical properties of **FTn** ($n = 1–5$) in CH₂Cl₂ are depicted in Figures 1 and 2, and summarized in Table 1. All the UV–vis spectra consisted of two absorption
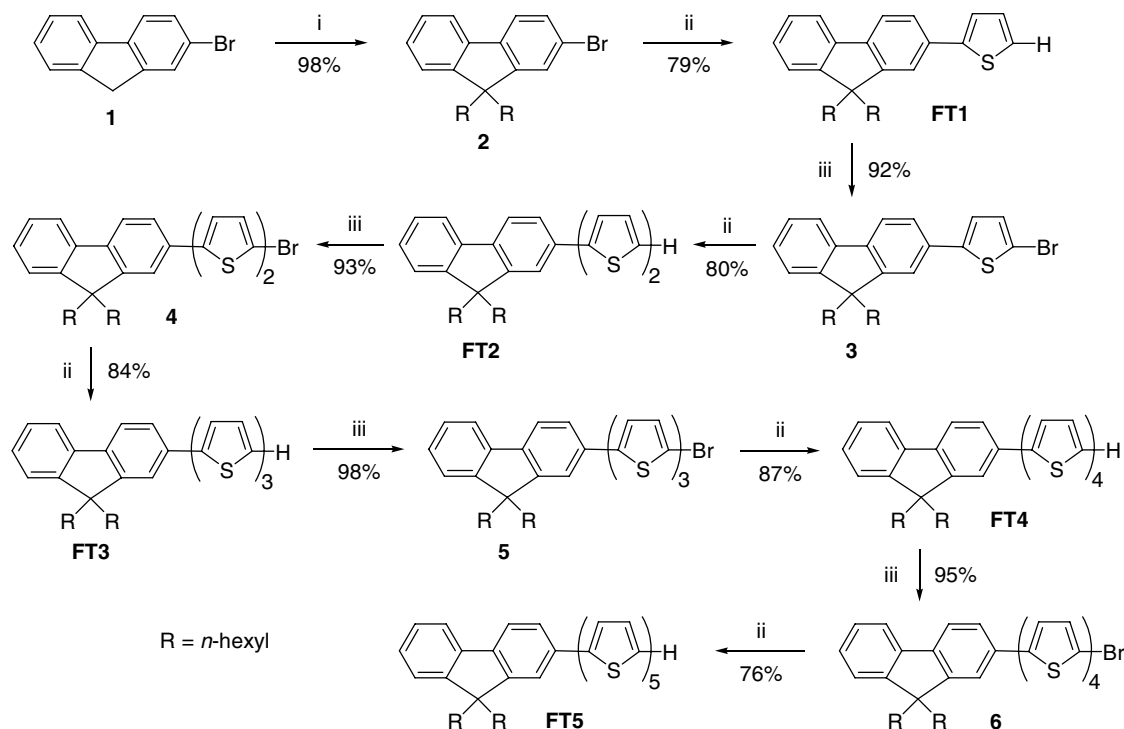
**Scheme 1.** Synthesis of **FTn** ($n = 1$–5). Reagents and conditions: (i) $n$-$C_6H_{13}Br$, $n$-$Bu_4NCl$, 50% NaOH, DMSO; (ii) 2-thiopheneboronic acid, Pd(PPh$_3$)$_4$, 2 M Na$_2$CO$_3$, THF, reflux; (iii) NBS, THF.
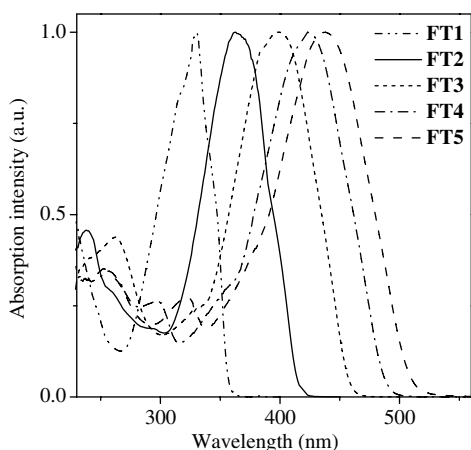


**Figure 1.** Absorption spectra of **FTn** ($n = 1$–5) in CH$_2$Cl$_2$.
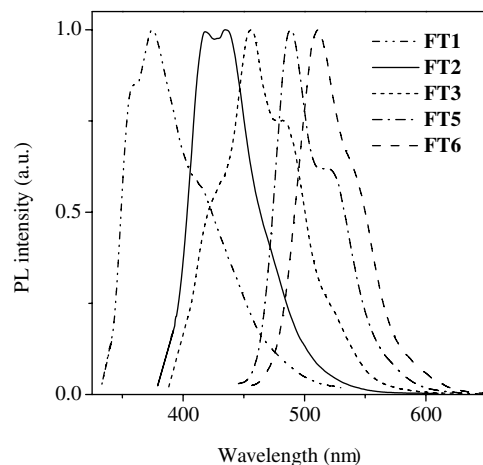


**Figure 2.** Photoluminescence (PL) spectra of **FTn** ($n = 1$–5) in CH$_2$Cl$_2$.

bands, which were assigned in terms of the strong absorption band at longer wavelength corresponding to the π–π* electron transition of the entire conjugated backbone and the less intense absorption bands originating from the π–π* local electron transition of the individual aromatic units. As expected, the intensity and absorption maxima of the former bands of **FTn** ($n = 1$–5) progressively increased and were red-shifted with increasing number of thiophene rings. Compounds **FTn** ($n = 1$–5) exhibited maximum absorptions at 330, 362, 398, 423, and 439 nm, which are considerably red-shifted relative to those of thiophene, bithiophene (302),[14] terthiophene (355),[15] quaterthiophene (390),[16] and quinquethiophene (416),[15] respectively. The elec-

tronic absorption maxima for **FT5** (439 nm) are quite close to that of regioregular poly(3-octylthiophene) (434 nm),[17] while its regiorandom polymer (428 nm)[18] has a similar electronic absorption band to that of the **FT4** (423 nm). These results suggested the formation of a highly extended π-electron delocalization system through the fluorene platform. The HOMO–LUMO energy gaps ($E_g$) (Table 1), estimated from the onset absorption edge, decrease with an increase in the π-conjugation length of the oligothiophene units. The photoluminescence (PL) spectra of **FTn** ($n = 1$–5) also showed a gradual red-shift of the maximum emission peak with increased number of thiophene rings. Moreover, an excellent linear correlation of the absorption and emis-

**Table 1.** Summary of the physical data of **FTn** ($n = 1$–5)

| Compound | $\lambda_{abs}$/nm ($\log \varepsilon$/dm$^3$/mol cm)[a] | $\lambda_{em}$/nm[b] | $E_g$/eV[c] | $E_{1/2}$/V ($\Delta E$/mV)[d] | $T_c/T_m/T_d$/°C[e] | HOMO/eV[g] | LUMO/eV[h] |
|---|---|---|---|---|---|---|---|
| **FT1** | 330 (4.59) | 374 | 3.48 | <u>1.02</u> (200), 1.28 (170) | NA | −5.65 | −2.17 |
| **FT2** | 362 (4.83) | 418, 434 | 2.99 | <u>0.85</u> (50), 1.09 (150) | NA | −5.48 | −2.49 |
| **FT3** | 398 (5.11) | 456, 481 | 2.71 | <u>0.77</u> (60), 0.99 (150) | 53/105/406 | −5.36 | −2.65 |
| **FT4** | 423 (5.34) | 488, 514 | 2.54 | 0.87 (70), 1.16 (100) | 127[f]/172/417 | −5.25 | −2.71 |
| **FT5** | 439 (5.77) | 516 | 2.44 | 0.83 (70), 1.09 (90) | 190[f]/225/420 | −5.22 | −2.78 |

The underlined values refer to an unresolved and irreversible process.
[a] Measured in dilute CH$_2$Cl$_2$ solution.
[b] Excited at the absorption maxima.
[c] Estimated from the onset of absorption spectra ($E_g = 1240/\lambda_{onset}$).
[d] Measured using a platinum rod counter electrode, a glassy carbon working electrode, and a SCE reference electrode in CH$_2$Cl$_2$ containing $n$-Bu$_4$NPF$_6$ as a supporting electrolyte with a scan rate of 50 mV/s under an argon atmosphere.
[e] Obtained from DSC measurements during the second heating cycle with a heating rate of 10 °C/min under N$_2$.
[f] Observed upon cooling.
[g] Calculated by the empirical equation: HOMO $= -(4.44 + E_{onset})$.
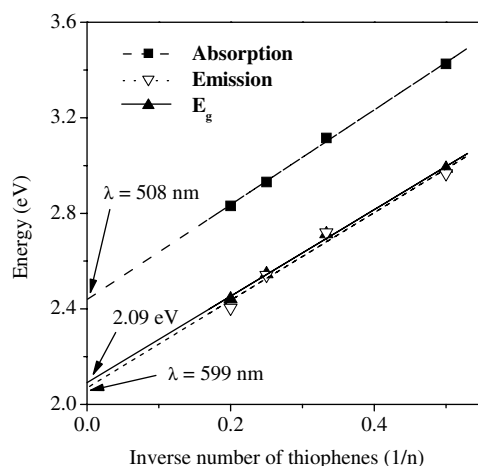[h] Calculated from LUMO = HOMO + $E_g$.



**Figure 3.** Plots of absorption and emission maxima, and energy gap ($E_g$) for **FTn** ($n = 2$–5) in CH$_2$Cl$_2$ with the inverse number of thiophene rings ($1/n$).



**Figure 4.** CV curves of **FTn** ($n = 1$–5) in CH$_2$Cl$_2$ at a scan rate of 50 mV/s.

sion maxima, and energy gaps ($E_g$) with the inverse number of thiophene rings for the fluorene platform series in CH$_2$Cl$_2$ was observed (Fig. 3). Extrapolation to a hypothetical infinite number of thiophene rings models the properties of an ideal polymer (in solution) and gives a maximum absorption at 508 nm, a maximum emission at 599 nm and an energy gap ($E_g$) of 2.09 eV. These values are lower than those found experimentally for polythiophene film (solid) due to defects and interruptions of the conjugated backbone in the polymer. However, on the basis of the spectroscopic investigation of oligothiophenes, the effective conjugation length is not much longer than 15–20 thiophene units.[19,20] Therefore, this correlation allows an estimation of the mean conjugation length in the real polymer, which is in this case for a polythiophene of about 20 thiophene units and thus differs significantly from the mean conjugation length of the polymer.

Cyclic voltammetry (CV) was performed to investigate the redox properties of **FTn** ($n = 1$–5). The results are shown in Figure 4 and are summarized in Table 1. On increasing the number of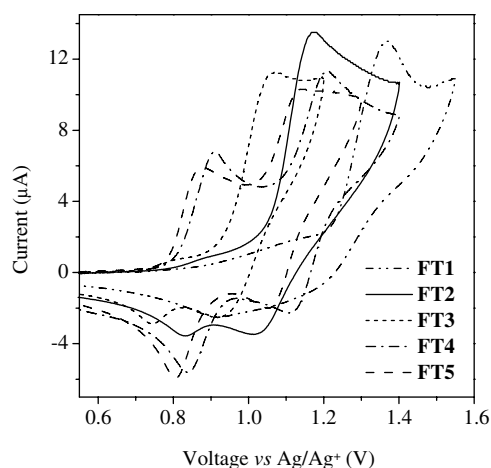 thiophene rings, the oxidation curves were gradually shifted to a lower oxidation potential. This is in accord with the longer conjugation length achieved.[21] The CV curves of compounds **FT1**, **FT2**, and **FT3** demonstrated one oxidation process at 1.28, 1.09, and 0.99 V, respectively, corresponding to the removal of electrons from the terminal thiophene ring to form the radical cation and a weak oxidation process at lower potential (1.02, 0.85, and 0.77 V, respectively) corresponding to the removal of electrons from the dimer originating from an oxidative coupling of the radical cation. However, compounds **FT4** and **FT5** behaved totally differently and exhibited two reversible oxidation processes at 0.87 and 1.16 V, and 0.83 and 1.09 V, respectively. The first oxidation process corresponds to the removal of an electron from the terminal thiophene ring and the second oxidation process can be assigned to the removal of electrons from the interior moieties. Upon repeated scanning, there was no weak oxidation process due to an oxidative coupling at lower potential being observed. This result indicates that radical cations for the tetramer and pentamer are stable to an oxidative coupling and the radical cations of shorter oligomers ($n \leqslant 3$) tend to dimerize inherently. In addition, no obvious reduction process was detected

in all cases. The HOMO and LUMO energy levels of the oligomers were determined using the onset positions of the oxidation and energy gap ($E_g$) and are summarized in Table 1.

The thermal properties of oligomers **FTn** ($n = 3$–5) were investigated by differential scanning calorimetry (DCS). All were found to be thermally stable, with the onset of decomposition temperatures above 406 °C under nitrogen. The results are summarized in Table 1. As expected, the increasing number of thiophene rings resulted in an increase of the phase transition temperatures. The DSC curves of samples recrystallized from $CH_2Cl_2$/methanol exhibited clear endothermic melting peaks ($T_m$) during the first heating scan at 105, 172, and 225 °C, respectively. On subsequent cooling, only compounds **FT4** and **FT5** were found to recrystallize with the recrystallization temperatures ($T_c$) being observed at 127 and 190 °C, respectively. When the non-recrystallized sample **FT3** was reheated, the second DSC curve showed an exothermic crystallization peak ($T_c$) at 53 °C followed by an endothermic peak due to melting of the same crystalline form at 105 °C. In the cases of **FT4** and **FT5**, only sharp endothermic melting peaks ($T_m$) were detected during the second heating scan at 172 and 225 °C, respectively.

In conclusion, we have presented a convenient and efficient synthetic approach to a series of α-fluorenyl oligothiophenes up to the pentamer using Suzuki cross-coupling and bromination reactions. The presence of the fluorene offers good solubility and extends the π-electron delocalization system of the oligomers. Substantially red-shifted absorption and emission spectra, improved transition temperatures and decreased oxidation potentials of the oligomers were observed as more thiophene rings were introduced. The tetramer and pentamer were crystalline and stable to electrochemically oxidative dimerization.

### Acknowledgments

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13. Characterization data. Compound **FT1**: light green viscous oil; IR (KBr) 2927, 1467, 1214, 1052, 808, and 693 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) δ 0.73–0.78 (4H, m), 0.81–0.86 (6H, m), 1.12–1.22 (12H, m), 2.05–2.10 (4H, m), 7.15 (1H, dd, $J = 5.1$ Hz, $J = 3.6$ Hz), 7.33–7.45 (5H, m), 7.66–7.69 (2H, m), and 7.74–7.77 (2H, m); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 14.04, 22.62, 23.79, 31.52, 40.47, 55.21, 119.75, 120.08, 120.24, 122.87, 122.91, 124.47, 124.94, 126.87, 127.15, 128.05, 133.25, 140.70, 140.78, 150.94, and 151.57; HRMS-ESI *m/z*: [MH$^+$] calcd for C$_{29}$H$_{37}$S$_1$ 417.2610; found, 417.2618.
Compound **FT2**: green viscous oil; IR (KBr) 2927, 1467, 1212, 1054, 809, and 691 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) δ 0.68–0.70 (4H, m), 0.79 (6H, t, $J = 7.0$ Hz), 1.09–1.17 (12H, m), 2.02 (4H, t, $J = 8.0$ Hz), 7.07 (1H, t, $J = 4.3$ Hz), 7.20 (1H, d, $J = 3.9$ Hz), 7.25 (2H, d, $J = 3.9$ Hz), 7.31 (1H, d, $J = 3.9$ Hz), 7.35–7.38 (3H, m), 7.57 (1H, d, $J = 1.0$ Hz), 7.60 (1H, dd, $J = 7.9$ Hz, $J = 1.6$ Hz), and 7.70 (2H, dd, $J = 8.0$ Hz, $J = 2.2$ Hz); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 13.90, 22.56, 23.74, 29.69, 31.47, 40.41, 55.18, 119.72, 119.85, 120.08, 122.88, 123.46, 123.54, 124.29, 124.55, 124.63, 126.84, 127.16, 127.87, 132.83, 136.35, 137.58, 140.59, 140.89, 144.02, 150.60, and 151.91; HRMS-ESI *m/z*: [MH$^+$] calcd for C$_{33}$H$_{39}$S$_2$ 499.2488; found, 499.2496.
Compound **FT3**: yellow solid; mp 105 °C; IR (KBr) 2930, 1467, 1214, 1050, 810, and 692 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) δ 0.66–0.70 (4H, m), 0.78 (6H, t, $J = 6.8$ Hz), 1.08–1.16 (12H, m), 2.01 (4H, t, $J = 8.5$ Hz), 7.04 (1H, dd, $J = 5.1$ Hz, $J = 3.6$ Hz), 7.13 and 7.14 (2H, AA′BB′, $J = 3.7$ Hz), 7.19 (1H, d, $J = 3.9$ Hz), 7.20 (1H, dd, $J = 3.7$ Hz, $J = 1.2$ Hz), 7.24 (1H, dd, $J = 5.1$ Hz, $J = 1.2$ Hz), 7.31 (1H, d, $J = 3.9$ Hz), 7.33–7.37 (3H, m), 7.56 (1H, d, $J = 1.2$ Hz), 7.59 (1H, dd, $J = 7.9$ Hz, $J = 1.5$ Hz), and 7.70 (2H, d, $J = 8.1$ Hz); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 13.96, 22.54, 23.72, 29.67, 31.45, 40.39, 55.17, 119.71, 119.84, 120.08, 122.88, 123.55, 123.70, 124.07, 124.42, 124.50, 124.53, 124.57, 126.83, 127.17, 127.89, 132.72, 135.98, 136.25, 137.58, 140.59, 140.99, 144.18, 150.91, and 151.92; HRMS-ESI *m/z*: [MH$^+$] calcd for C$_{37}$H$_{41}$S$_3$ 581.236; found, 581.2372.
Compound **FT4**: orange yellow solid; mp 172 °C; IR (KBr) 2928, 1469, 1214, 1050, 807, and 691 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) δ 0.65–0.71 (4H, m), 0.78 (6H, t, $J = 6.8$ Hz), 1.08–1.17 (12H, m), 2.02 (4H, t, $J = 8.0$), 7.04 (1H, dd, $J = 5.1$ Hz, $J = 3.6$ Hz), 7.12–7.16 (4H, m), 7.21 (2H, t, $J = 3.0$ Hz), 7.24 (1H, d, $J = 4.8$ Hz), 7.31 (1H, d, $J = 3.9$ Hz), 7.33–7.37 (3H, m), 7.57 (1H, s), 7.59 (1H, dd, $J = 7.8$ Hz, $J = 1.2$ Hz), and 7.70 (2H, d, $J = 7.8$ Hz); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 13.96, 22.55, 23.73, 29.68, 31.46, 40.40, 55.18, 119.72, 119.84, 120.09, 122.88, 123.59, 123.78, 124.15, 124.25, 124.36, 124.42, 124.58, 124.65, 126.84, 127.19, 127.91, 132.70, 135.80, 135.92, 136.38, 136.48, 137.07, 140.54, 140.98, 144.26, 150.92, and 151.92;

HRMS-ESI $m/z$: [MH$^+$] calcd for $C_{41}H_{43}S_4$ 663.2242; found, 663.2230.

Compound **FT5**: red yellow solid; mp 225 °C; IR (KBr) 2927, 1466, 1214, 1053, 805, and 692 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 0.66–0.68 (4H, m), 0.78 (6H, t, $J = 7.0$ Hz), 1.08–1.16 (12H, m), 2.01 (4H, t, $J = 8.2$ Hz), 7.05 (1H, t, $J = 3.9$ Hz), 7.09–7.14 (6H, m), 7.20 (2H, br s), 7.24 (1H, d, $J = 5.1$ Hz), 7.31–7.37 (4H, m), 7.56 (1H, s), 7.59 (1H, d, $J = 8.1$ Hz), and 7.70 (2H, d, $J = 7.8$ Hz); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 14.00, 22.57, 23.73, 29.69, 31.47, 40.41, 55.17, 119.74, 119.82, 120.11, 122.88, 123.60, 123.80, 124.18, 124.28, 124.34, 124.43, 124.54, 124.67, 126.84, 127.20, 127.93, 132.75, 135.82, 135.92, 136.00, 136.38, 136.49, 137.05, 140.53, 141.10, 144.24, 150.90, and 151.61; HRMS-ESI $m/z$: [MH$^+$] calcd for $C_{44}H_{45}S_5$ 741.3140; found, 741.1334.

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