1. Synthesis of a Segmented Liquid-Crystalline Polymer Having Side-Chain Terpyidine Group (PTBP)

In this study, we synthesized a segmented main-chain liquid-crystalline polymer having side-chain terpyidine group (PTBP), the reaction route of which is shown in Scheme 1.

**Scheme 1. Synthesis Route for PTBP**

*Synthesis of 1,5-bis(2′-bipyridyl)pentane-1,3,5-trione (I).* A solution of acetone (1.8 mL, 25 mmol) and ethyl 2-pyridine-carboxylate (10.1 mL, 75 mmol) in dry tetrahydrofuran (THF) (50 mL) was added dropwise to a refluxing suspension of sodium hydride (95%, 1.9 g, 75 mmol) in dry THF (50 mL) under a nitrogen atmosphere for 4 h. After an additional reflux for 2 h, the THF was removed under a reduced
pressure and the remaining orange-color paste was carefully washed with water (100 mL). The resultant orange-color solution was filtered through Celite and the pH of the filtrate was adjusted to 7 by the dropwise addition of 5% acetic acid. The resultant yellowish solid was collected, washed with water, and dried. The material was then recrystallized from ethanol to obtain 5.1 g of yellowish product. Yield = 75%. $^1$H NMR (δ, CDCl$_3$): 4.45 (s), 6.94 (s), 6.99 (s), 7.38-7.50 (m), 7.81-7.92 (m), 8.01-8.12 (m), 8.67-8.75 (m). FTIR (KBr, cm$^{-1}$): v3140, 1612, 1572, 1442, 1378, 1276, 1146, 1084, 988, 940, 872, 838, 786, 736, 646, 586.

**Synthesis of 2,6-bis(2′-pyridyl)-4-pyridone (II).** A solution of I (2.0 g, 7.46 mmol) and ammonium acetate (4.0 g, excess) in ethanol (50 mL) was heated and refluxed overnight, after which the dark brownish solution was concentrated to half volume. The solution was cooled and the white-color precipitate was collected by filtration and washed well with diethyl ether. Recrystallization from ethanol produced 1.35 g of white product. Yield: 75%. $^1$H NMR (δ, CDCl$_3$): 7.33 (m), 7.44 (m), 7.90 (m), 7.97 (m), 8.79 (m), 9.15 (NH). FTIR (KBr, cm$^{-1}$): v3276, 3054, 3004, 2240, 1820, 1630, 1578, 1512, 1472, 1432, 1364, 1256, 1204, 1084, 998, 942, 858, 786, 736, 700, 648, 620, 586, 540, 488.

In the synthesis of monomer III, monomer II (2.5 g, 10 mmol) and anhydrous powdered K$_2$CO$_3$ (10.4 g, 75 mmol) were dissolved in 100 mL of acetonitrile and the mixture was heated and refluxed for 2 h. Then, a solution of diethyl (5-bromopentyl)malonate (3.9 g, 12 mmol) dissolved in 50 mL of acetonitrile and a trace of potassium iodide was added to the above mixture and it was refluxed for 24 h. After filtration and evaporation of the solvent, the crude product was purified using silica gel column chromatography with hexane/ethyl acetate (2/3, v/v) as eluent, and then recrystallized from hexane/ethyl acetate (4/1, v/v) to obtain 3.1 g of white powder. Yield = 65%. m.p. = 63 °C. $^1$H NMR (δ, CDCl$_3$): 1.28 (t, 6H, -CH$_3$), 1.31–1.60 (m, 4H, -CH$_2$-), 1.78–2.0 (m, 4H, -CH$_2$-), 3.32 (t, 1H, -CH-), 4.18 (t, 4H, -CH$_2$CO-), 4.23 (t, 2H, -CH$_2$O-), 7.38 (t, 2H, Pyridyl-H), 7.90 (t, 2H, Pyridyl-H), 8.06 (s, 2H, Pyridyl-H), 8.65 (d, 2H, Pyridyl-H), 8.72 (d, 2H, Pyridyl-H).

PTBP was obtained via transesterification by melt polymerization using the following procedures. To a 3-neck 50 mL flask, equipped with an overhead condenser with an argon gas inlet and a vacuum line on the adapter, were added monomer III (1.91 g, 4 mmol), 4,4′-bis(6-hydroxy) biphenyl (1.55 g, 4 mmol),
the synthesis procedure of which has been described in our previous paper, and 0.2 wt % PbO. The mixture was heated to 170 °C under the flow of an argon gas. After stirring for 3 h, during which methanol was distilled off, the fluid began to be viscous. Then, the argon gas inlet was closed and the outlet was connected to a vacuum pump. The reaction mixture was heated at 170 °C for 4 h under a reduced pressure. Subsequently, the polymer was purified by dissolution in chloroform and precipitated twice in acetone. PTBP was found to have a number-average molecular weight \( M_n = 22,500 \) and a weight-average molecular weight \( M_w = 26,600 \), as determined by gel permeation chromatography (GPC, Waters) against polystyrene standards and THF as an eluent. Yield = 90 %. \(^1\)H NMR (\( \delta \), CDCl₃): 1.25-1.5 (m, 12H, -CH₂-), 1.52−1.9 (m, 12H, -CH₂-), 3.28 (t, 1H, -CH-), 3.88 (t, 4H, -CH₂O-), 4.06 (t, 4H, -CH₂O-), 4.22 (t, 2H, -CH₂O-), 6.80 (d, 4H, Ar-H), 7.38 (d, 6H, Ar-H and Pyridyl-H ), 7.90 (t, 2H, Pyridyl-H), 8.05 (s, 2H, Pyridyl-H), 8.65 (d, 4H, Pyridyl-H).

Figure 1 shows differential scanning calorimetry (DSC) thermograms of PTBP at a scanning rate of 20 °C/min during the heating and cooling cycles. It can be seen from Figure 1 that PTBP has a glass transition temperature (\( T_g \)) of 49.9 °C and a clearing temperature of 80.7 °C during heating. The POM

![Figure 1](image)

**Figure 1.** DSC thermograms of PTBP during (a) heating and (b) cooling cycles. The inset is the polarized optical microscopy (POM) image taken after annealing at 70 °C for 24 h.
image shown in the inset of Figure 1 indicates that PTBP has smectic mesophase at temperatures between 49.9 and 80.7 °C, and thus 80.7 °C represents a smectic-to-isotropic transition temperature. Interestingly, no evidence of crystallinity in PTBP can be observed from the DSC thermograms shown in Figure 1. We attribute this observation to the presence of bulky side-chain terpyridine groups in PTBP.

2. Synthesis of \([\text{Ru(II)(PTBP)(6TPy)}](\text{PF}_6)_2\) Complex

In the preparation of PTBP-ruthenium complex \([\text{Ru(II)(PTBP)(6TPy)}](\text{PF}_6)_2\) (hereafter referred to as PTBP-Ru-6TPy) following the reaction route shown in Scheme 2, we first synthesized a small-molecule terpyridine, \(1-(2,2':6', 2''\text{-terpyridyl}-4'-\text{oxy})\text{hexane}\) (hereafter referred to as 6TPy) using the following procedures: monomer \(\text{II}\) (2.5 g, 10 mmol) and anhydrous powdered \(\text{K}_2\text{CO}_3\) (6.9 g, 50 mmol) were dissolved in 50 mL of acetonitrile and the mixture was heated and refluxed for 2 h. Then, a solution of 1-bromohexane (2.5 g, 15 mmol) dissolved in 50 mL of acetonitrile and a trace of potassium iodide were added to the above.
mixture, which was then refluxed for 24 h. After filtration and evaporation of the solvent, the crude product was purified using silica gel column chromatography with hexane/ethyl acetate (3/2, v/v) as eluent, and then recrystallized from hexane/ethyl acetate (10/1, v/v) to obtain 1.65 g of needlelike product. Yield = 50%. $^1$H NMR (δ, CDCl$_3$): 0.90 (t, 3H, -CH$_3$), 1.30–1.55 (m, 6H, -CH$_2$-), 1.78–1.90 (m, 2H, -CH$_2$-), 4.25 (t, 2H, -CH$_2$O-), 7.38 (t, 2H, Pyridyl-H), 7.90 (t, 2H, Pyridyl-H), 8.04 (s, 2H, Pyridyl-H), 8.66 (d, 2H, Pyridyl-H), 8.72 (d, 2H, Pyridyl-H).

**Synthesis of 6TPy-RuCl$_3$ Monocomplex.** A solution of 6TPy in methanol (25 mL) was stirred at 60 °C, and then, an equimolar amount of RuCl$_3$·3H$_2$O was added to the solution. The reaction of the mixture was continued overnight. Subsequently, the reaction mixture was cooled to −20 °C. The resulting dark orange-color precipitate was collected by filtration and washed twice with ice water, followed by diethyl ether. Figure 2 gives the Fourier transform infrared (FTIR) spectra of 6TPy and 6TPy-RuCl$_3$ monocomplex. It can be seen in Figure 2 that the interaction of RuCl$_3$ with 6TPy has shifted the wavenumbers at 1560 and 1577 cm$^{-1}$ for C–N stretching to 1604 cm$^{-1}$, an enlarged section of which is

![Figure 2. FTIR spectra of (a) 6TPy and (b) 6TPy-RuCl$_3$ monocomplex. The Inset gives the absorption band from a wavenumber of 1500 to 1650 cm$^{-1}$.](image-url)
shown in the inset. It should be mentioned that the appearance of a strong absorption peak at a wavenumber of 3055 cm\(^{-1}\) (assigned to –CH– stretching in the pyridyl ring of 6TPy due to the influence of RuCl\(_3\)) for 6TPy-RuCl\(_3\) monocomplex is additional evidence confirming the successful coordination between 6TPy and RuCl\(_3\). Figure 3 gives the ultraviolet-visible (UV-vis) spectra of 6TPy in CHCl\(_3\) and 6TPy-RuCl\(_3\) monocomplex in N,N-dimethylformamide (DMF). The characteristic metal-to-ligand charge-transfer (MLCT) band for the mono(terpyridine) ruthenium (III) complex at a wavelength of about 405 nm can be observed in Figure 3. Further, we observe from Figure 3 that a characteristic bathochromic shift of the \(\pi-\pi^*\) absorption bands of the ligand occurs at wavelengths of approximately 279 and 310 nm. From the results of FTIR and UV-vis spectroscopy, we can conclude that 6TPy has successfully coordinated with RuCl\(_3\) and formed 6TPy-RuCl\(_3\) monocomplex.

![Figure 3. UV-vis spectra of (a) 6TPy in CHCl\(_3\) and (b) 6TPy-RuCl\(_3\) monocomplex in DMF.](image)

Synthesis of \([\text{Ru(II)}(\text{PTBP})(6\text{TPy})](\text{PF}_6)_2\) Complex (PTBP-Ru-6TPy). PTBP (0.77 g) and 6TPy-RuCl\(_3\) monocomplex (0.54 g, equimolar amount of terpyridine in PTBP) were mixed in 50 mL of a co-solvent of THF and ethanol (9:1, v/v). Five drops of N-ethylmorpholine were added and the mixture was heated and refluxed for 24 h under an argon gas atmosphere. After evaporation of about half of the
solvent, an excess of ammonium hexafluorophosphate (2.0 g, 13.8 mmol) was added and the mixture was cooled to 0 °C. The precipitate was removed by filtration and washed with a 60/40 (v/v) mixture of ethanol and water, and then dried in a vacuum oven at 100 °C for several days. Figure 4 shows FTIR spectra of PTBP and PTBP-Ru-6TPy. It can be seen from the inset of Figure 4 that the two absorption peaks at wavenumbers of 1562 and 1573 cm$^{-1}$ of C–N stretching for PTBP have been weakened in PTBP-Ru-6TPy, while a strong absorption peak appears at a wavenumber of 1610 cm$^{-1}$ for C–N stretching. The appearance of this new absorption peak presents evidence of the successful formation of ruthenium complex between 6TPy-RuCl$_3$ and PTBP.

![Figure 4](image)

**Figure 4.** FTIR of (a) PTBP and (b) PTBP-Ru-6TPy. The inset gives the absorption band from a wavenumber of 1500 to 1700 cm$^{-1}$.

Figure 5 shows UV-vis spectra for PTBP in chloroform (CHCl$_3$) and PTBP-Ru-6TPy in DMF. The characteristic MLCT band for the terpyridine ruthenium (II) complex at a wavelength of about 493 nm can be observed in Figure 5. In addition, it can be seen from Figure 5 that a characteristic bathochromic shift of the π–π* absorption bands of the ligand occurs at wavelengths of approximately 270 and 309 nm.

Figure 6 shows DSC thermograms of PTBP-Ru-6TPy at a scanning rate of 20 °C/min during the
heating and cooling cycles. It can be seen from Figure 6 that PTBP-Ru-6TPy only exhibits a $T_g$ of 123.4 °C during the heating cycle, which is 73.5 °C higher than the $T_g$ of PTBP (see Figure 1). POM images (not shown here) indicate that PTBP-Ru-6TPy does not exhibit liquid crystallinity, which is due to the increased bulky size of the side chain in PTBP and the strong interactions between ruthenium metal and 6TPy-RuCl₃.

![Figure 5](image1.png)

**Figure 5.** UV-vis spectra of (a) PTBP in CHCl₃ and (b) PTBP-Ru-6TPy in DMF.

![Figure 6](image2.png)

**Figure 6.** DSC thermograms of PTBP-Ru-6TPy during (a) heating and (b) cooling cycles.
3. Preparation of PTBP-Ru-6TPy/Organoclay Nanocomposites

In preparing nanocomposites based on PTBP-Ru-6TPy, for comparison we also employed two commercial organoclays (Southern Clay Products): (1) Cloisite 30B having a surfactant (MT2EtOH) with the chemical structure methylbis-2-hydroxyethyltallow alkyl quaternary ammonium chloride and (2) Cloisite 15A having a surfactant (2M2HT) with the chemical structure dimethyldihydrogenatedtallow alkyl quaternary ammonium chloride. The chemical structures of the surfactants, MT2EtOH and 2M2HT, are shown below:

\[
\begin{align*}
\text{MT2EtOH} & : \quad \text{CH}_3 \quad \text{N}^+ \quad \text{T} \\
\text{CH}_2\text{CH}_2\text{OH} \\
\text{CH}_5 \quad \text{N}^+ \quad \text{HT} \\
\text{CH}_2\text{CH}_2\text{OH} \\
\text{2M2HT} & : \quad \text{CH}_3 \\
\end{align*}
\]

In the chemical structure of MT2EtOH, N\(^+\) denotes quaternary ammonium chloride and T denotes tallow consisting of about 65% C18, about 30% C16, and about 5% C14, and in the chemical structure of 2M2HT, N\(^+\) denotes quaternary ammonium chloride and HT denotes hydrogenated tallow consisting of about 65% C18, about 30% C16, and about 5% C14. Note that 100% of Na\(^+\) ions in natural clay (montmorillonite, MMT) have been exchanged. Organoclay nanocomposites were prepared by solution blending; namely, a predetermined amount of PTBP-Ru-6TPy was dissolved in a co-solvent of DMF and H\(_2\)O (10:1, v/v) and then Cloisite 30B or Cloisite 15A suspended in a co-solvent of DMF and H\(_2\)O (10:1, v/v) was added slowly, under vigorously stirring, into the polymer solution. The solvent in the mixture was evaporated slowly under constant stirring for 2 days. Nanocomposites were dried completely in a vacuum oven at 100 °C until no weight change was detected. The amount of organoclay used was 5 wt % in all nanocomposites. Since the amount of surfactant MT2EtOH (or 2M2HT) residing at the surface of Cloisite 30B (or Cloisite 15A) is 32 wt %, the net amount of clay in each nanocomposite is 3.4 wt %.

Figure 7 shows X-ray diffraction (XRD) patterns of Cloisite 30B, Cloisite 15A, (PTBP-Ru-6TPy)/
(Cloisite 30B) nanocomposite, and (PTBP-Ru-6TPy)/(Cloisite 15A) nanocomposite. It can be seen in Figure 7 that the $d$-spacing of Cloisite 30B aggregates in (PTBP-Ru-6TPy)/Cloisite 30B nanocomposite

**Figure 7.** (a) XRD patterns of (1) Cloisite 30B and (2) Cloisite 15A, and (b) XRD patterns of (1) (PTBP-Ru-6TPy)/(Cloisite 30B) nanocomposite and (2) (PTBP-Ru-6TPy)/(Cloisite 15A) nanocomposite.
has only increased from 1.9 to 4.4 nm, and the $d$-spacing of Cloisite 15A aggregates in (PTBP-Ru-6TPy)/(Cloisite 15A) nanocomposite has slightly increased from 3.1 to 3.5 nm. We can speculate from the above observations that there would be poor dispersion of the organoclay, Cloisite 30B or Cloisite 15A, in the matrix of PTBP-Ru-6TPy. This speculation is indeed borne out to be the case, as evidenced from the TEM images shown in Figure 8; namely, (PTBP-Ru-6TPy)/(Cloisite 30B) nanocomposite has a flocculated structure while (PTBP-Ru-6TPy)/(Cloisite 15A) nanocomposite has an intercalated structure. This means that the chance of direct interactions between the positively charged ruthenium center in PTBP-Ru-6TPy and the negatively charged clay surface has been largely diminished, because of the shielding effect of positively charged surfactants. That is, the Coulombic interactions between the positively charged ruthenium center in PTBP-Ru-6TPy and the negatively charged clay surfaces, which exist in the (PTBP-Ru-6TPy)/MMT nanocomposite, are absent in the (PTBP-Ru-6TPy)/(Cloisite 30B) and (PTBP-Ru-6TPy)/(Cloisite 15A) nanocomposites.

Figure 8. TEM images of (a) (PTBP-Ru-6TPy)/(Cloisite 30B) nanocomposite and (b) (PTBP-Ru-6TPy)/(Cloisite 15A) nanocomposite.
Figure 9 gives the UV-vis spectra of thin films of PTBP-Ru-6TPy, (PTBP-Ru-6TPy)/(Cloisite 15A) nanocomposite, and (PTBP-Ru-6TPy)/(Cloisite 30B) nanocomposite. It can be seen from Figure 9 that the position of the MLCT band at a wavelength of about 493 nm for PTBP-Ru-6TPy has only slightly red-shifted to a wavelength of 508 nm for (PTBP-Ru-6TPy)/(Cloisite 15A) nanocomposite, and to a wavelength of 516 nm for (PTBP-Ru-6TPy)/(Cloisite 30B) nanocomposite. The $\pi-\pi^*$ band at a wavelength of 272 nm for PTBP-Ru-6TPy has decreased to a wavelength of 269 nm for both (PTBP-Ru-6TPy)/(Cloisite 15A) and (PTBP-Ru-6TPy)/(Cloisite 30B) nanocomposites. In the text, we have described that both red-shifted amount of MLCT band and the reduced amount of $\pi-\pi^*$ band increased giving rise to a very high degree of exfoliation of MMT aggregates in the matrix of PTBP-Ru-6TPy. We have attributed such experimental observations to the presence of the Coulombic interactions between the positively charged ruthenium center and the negatively charged MMT surfaces. If this kind of Coulombic interactions were absent or very small due to the shielding effect of a surfactant (MT2EtOH or 2M2HT) residing at the surface of Cloisite 30B or Cloisite 15A, a high degree of exfoliation of organoclay aggregates in (PTBP-Ru-6TPy)/(Cloisite 30B) and (PTBP-Ru-6TPy)/(Cloisite 15A) nanocomposites would not be possible.

Figure 9. UV-vis spectra of thin films of (a) PTBP-Ru-6TPy, (b) (PTBP-Ru-6TPy)/(Cloisite 15A) nanocomposite, and (c) (PTBP-Ru-6TPy)/Cloisite 30B nanocomposite.
Figure 10 shows FTIR spectra of MMT, Cloisite 15A, and Cloisite 30B. It can be seen from Figure 10 that these three clays all have an absorption peak at a wavenumber of 3625 cm$^{-1}$. The band at 3433 cm$^{-1}$ indicated in Figure 11a is assigned to the H–OH hydrogen bonded water. Notice in Figure 11c that the hydroxyl groups in the surfactant MT2EtOH residing at the surface of Cloisite 30B have an absorption peak at a wavenumber of 3410 cm$^{-1}$. Figure 11 shows the FTIR spectra of (PTBP-Ru-6TPy)/(Cloisite 15A) and (PTBP-Ru-6TPy)/(Cloisite 30B) nanocomposites. When compared with the FTIR spectrum of (PTBP-Ru-6TPy)/MMT nanocomposite (see the inset of Figure 3 in the text), we observe from the inset of Figure 11 that both (PTBP-Ru-6TPy)/(Cloisite 15A) and (PTBP-Ru-6TPy)/(Cloisite 30B) nanocomposites exhibit a very small absorption peak at a wavenumber of 1680 cm$^{-1}$, suggesting that little or no Coulombic interactions took place between the positively charged ruthenium center and the surface of organo clay (Cloisite 30B or Cloisite 15A) aggregates in the respective organo clay nanocomposites. This observation is in consonance with the conclusion drawn above from the UV-vis spectra (see Figure 9) of the (PTBP-Ru-6TPy)/(Cloisite 15A) and (PTBP-Ru-6TPy)/(Cloisite 30B) nanocomposites.

![FTIR spectra](image)

**Figure 10.** FTIR spectra of (a) MMT, (b) Cloisite 15A, and (c) Cloisite 30B.
Referring to Figure 11, (PTBP-Ru-6TPy)/(Cloisite 15A) nanocomposite shows a broad absorption peak at a wavenumber of about 3560 cm\(^{-1}\), which is very close to the absorption peak at about 3625 cm\(^{-1}\) for Cloisite 15A (see Figure 10b). Also, we observe in Figure 11 that (PTBP-Ru-6TPy)/(Cloisite 30B) nanocomposite shows an absorption peak at a wavenumber of 3415 cm\(^{-1}\), which is very close to the absorption peak at about cm\(^{-1}\) for the hydroxyl groups in the surfactant MT2EtOH residing at the surface of Cloisite 30B (see Figure 10c). The above observations seem to reinforce our conclusion drawn above that little interactions took place between the positively charged ruthenium center and the surface of Cloisite 15A (or Cloisite 30B) aggregates in the respective nanocomposites, owing to the shielding effect of a surfactant (MT2EtOH or 2M2HT) residing at the surface of Cloisite 30B or Cloisite 15A aggregates.

**Figure 11.** FTIR spectra of (a) (PTBP-Ru-6TPy)/(Cloisite 15A) nanocomposite, and (b) (PTBP-Ru-6TPy)/(Cloisite 30B) nanocomposite. The inset shows the expanded absorption band at wavenumbers ranging from 1500 to 1800 cm\(^{-1}\).
References: