

CHAPTER III

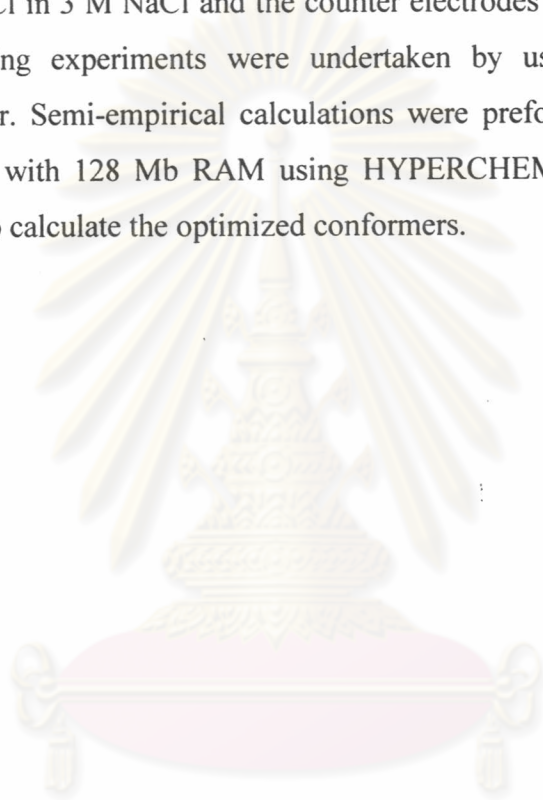
EXPERIMENTAL SECTION

3.1 General materials and instruments

All reagents were purchased from Aldrich Chemical Co. and Fischer Chemical Co. Potassium carbonate and cuprous cyanide were ground and dried at 100°C under reduced pressure overnight before use. Tetrahydrofuran (THF) was freshly distilled from sodium/benzophenone. Toluene was dried with magnesium sulfate overnight and distilled before use. Carbon tetrachloride was dried by simple distillation before use, rejecting the first 10 % percent of distillate; until the distillate is clear (bp. 77°C). *N*-bromosuccinimide (NBS) was recrystallized from hot water. The crystals were then allowed to dry at room temperature in the dark. The inhibitor was removed from the methylmethacrylate (MMA) by washing twice with equal amount of 10% NaOH solution. The MMA was then washed with distilled water until the base had been removed. The MMA was then dried over sodium sulfate anhydrous and evaporated under reduced pressure. Bisphenol A was recrystallized from methanol.

¹H NMR and ¹³C NMR spectra were recorded on Varian Mercury 400 and 100 MHz spectrometer. Deuterated chloroform was used as the solvent, and chemical shift values (δ) were reported in parts per million (ppm) relative to the residual signals of this solvent (δ 7.24 for ¹H and δ 77.0 for ¹³C). Infrared spectra were acquired using an Impact 410 Nicolet FT-IR spectrometer as a solid suspended in a potassium bromide disk between 600 and 3500 cm⁻¹ in transmittance mode. Mass spectroscopy was determined using FISIONS Instrument Mass spectrometer model Trioto 2000 in EI mode at 70 eV. Melting points were measured using an Electrothermal 9100 melting point apparatus. UV-vis absorption spectra were recorded on a Varian Carry Eclipse using 1 cm path length quartz cells. Fluorescence emission spectra were measured using Varian Cary Eclipse. The fluorescence quantum yield (ϕ_f) was determined at 298 K in tetrahydrofuran against anthracene in ethanol as the standard (0.27). Elemental analyses were recorded on CHNS/O ANALYZER (Perkin Elmer PE2400 Series II). Thermogravimetric analyses (TGA) were carried out under nitrogen at a heating rate

of 10°C/min using a TA instrument model 2950 thermogravimetric analyzer. Gel permeation chromatography (GPC) was carried out on a Jasco 880-PU system with Jasco UV-970 Detector. Calibration was done with standard polystyrene samples. Tetrahydrofuran was used as the eluent at a flow rate of 1 mL min⁻¹ at 28°C. All cyclic voltammograms were recorded on NIKKO KEISOKU Potentiogalvanostat NPGFZ-2501-A and exact function generator for voltage control. The working electrode used was a 1.6 mm diameter Carbon black electrode, the reference electrode used was a Ag/AgCl in 3 M NaCl and the counter electrodes used was Pt gauze. The scintillation counting experiments were undertaken by using NE LSC-2 liquid scintillation counter. Semi-empirical calculations were performed on a Pentium IV personal computer with 128 Mb RAM using HYPERCHEM, version 6. The AM1 method was used to calculate the optimized conformers.

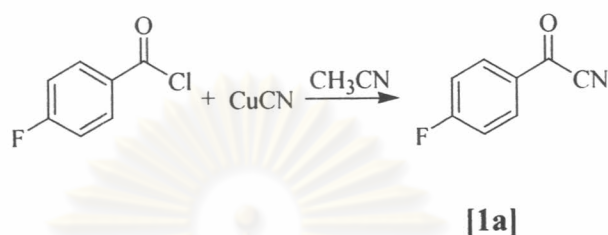


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Part A: Preparation of free-radical polymers

3.2 Preparation of benzoyl cyanide derivatives

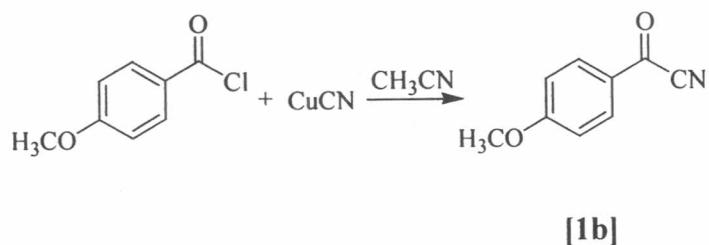
3.2.1 Synthesis of 4-fluorobenzoyl cyanide



4-Fluorobenzoyl chloride (6.00 mL, 50 mmol), cuprous cyanide (6.72 g, 75 mmol) and dry acetonitrile (50 mL) were added to a three-neck round bottom flask equipped with condenser and nitrogen inlet. The mixture was heated at 80°C for 4 hours. Then acetonitrile was removed by vacuum evaporation. The remaining mixture was extracted by toluene and decolorized by using activated charcoal. The product was purified by distillation at 114-116°C under reduced pressure to give 4-fluorobenzoyl cyanide as a colorless liquid (6.33 g, 85 %). FT-IR spectrum (KBr pellet): ν 3075 (w, arom. C-H), 2223 (m, cyanide), 1689 (s, arom. C=O), 1591 (s, arom. C=C), 1242 (m, C-F stretching) cm^{-1} ; $^1\text{H-NMR}$ spectrum (CDCl_3): δ 8.25- 8.22 (dd, 2H, $J = 8.0$ Hz), 7.35- 7.31 (dd, 2H, $J = 8.0$ Hz) ppm; $^{13}\text{C-NMR}$ spectrum (CDCl_3): δ 170.0, 166.3, 133.8, 130.3, 117.8, 116.3, 112.8 ppm; MS m/z : 149 M^+ ; Anal. Calcd for $\text{C}_8\text{H}_4\text{FNO}$: C, 64.43; H, 2.70; N, 9.39; Found: C, 64.33; H, 2.51; N, 9.44.

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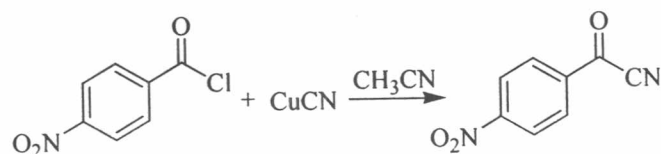
3.2.2 Synthesis of 4-methoxybenzoyl cyanide



By using the same procedure as described for **[1a]**, 4-methoxybenzoyl chloride (5.40 mL, 50 mmol), was used instead of 4-fluorobenzoyl chloride. The product was obtained as a colorless solid (4.03 g, 50 %): FT-IR spectrum (KBr pellet): ν 2991 (w, arom. C-H), 2217 (m, cyanide), 1782 (s, arom. C=O), 1675, 1506 (s, arom. C=C) cm^{-1} ; $^1\text{H-NMR}$ spectrum (CDCl_3): δ 8.15- 8.13 (m, 2H), 7.09- 7.07 (m, 2H), 3.98 (s, 3H) ppm; $^{13}\text{C-NMR}$ spectrum (CDCl_3): δ 190.0, 167.8, 130.7, 129.0, 117.2, 116.0, 114.6, 56.0; MS m/z : 161 M^+ ; Anal. Calcd for $\text{C}_9\text{H}_7\text{NO}_2$: C, 67.07; H, 4.38; N, 8.69; Found: C, 67.03; H, 4.41; N, 8.64; mp.= 58-60°C.

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3.2.3 Synthesis of 4-nitrobenzoyl cyanide



[1c]

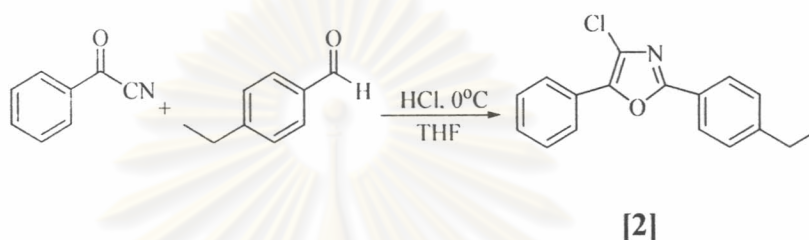
By using the same procedure as described for [1a], 4-nitrobenzoyl chloride (9.27, 50 mmol) was used instead of 4-fluorobenzoyl cyanide. The product was obtained as a yellow solid (7.92 g, 90 %): mp. 106-108°C; FT-IR spectrum (KBr pellet): ν 3111 (w, arom. C-H), 2223 (m, cyanide), 1683 (s, arom. C=O), 1529 (s, arom. C=C), 1350 (w, C-N) cm^{-1} ; ¹H-NMR spectrum (CDCl₃): δ 8.40- 8.28 (m, 4H) ppm; ¹³C-NMR spectrum (CDCl₃): δ 166.0, 159.7, 137.4, 133.5, 131.8, 124.7, 123.6, 112.3; MS m/z : 176 M⁺; Anal. Calcd for C₈H₄N₂O₃: C, 54.54; H, 2.29; N, 15.91; Found: C, 54.57; H, 2.31; N, 15.86.

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3.3 Preparation of 4-chloro-5-phenyl-2-(4'-vinylphenyl)oxazole

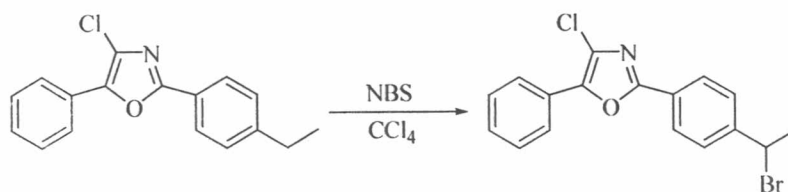
The synthesis of 4-chloro-5-phenyl-2-(4'-vinylphenyl)oxazole involved the following three steps:

3.3.1 Preparation of 4-chloro-2-(4'-ethylphenyl)-5-phenyloxazole



Benzoyl cyanide (2.62 g, 20 mmol) and 4-ethylbenzaldehyde (2.68 g, 20 mmol) in 50 mL dry THF were contained in reaction flask. The reaction flask was then connected to a HCl gas generator. The reaction mixture was allowed to cool in an ice-NaCl cooling bath and then dry HCl gas passed into the solution flask until the HCl gas was no longer absorbed by the reaction mixture, tested by ammonia at the outlet of the reaction flask. At this stage, the reaction flask was quickly sealed and kept at 0°C for 2 days. The reaction mixture was then poured onto an ice with continuous stirring and extracted with methylene chloride (2×25 mL). The organic layer was washed with water (2×15 mL), saturated sodium bisulfite solution (2×10 mL) and then dried over magnesium sulfate. This solution was evaporated to dryness under reduced pressure to yield the crude product as a pale yellow solid. The solid was then recrystallized from ethyl acetate to give 4-chloro-2-(4-ethylphenyl)-5-phenyloxazole as a colorless solid (3.70 g, 65 %): mp. 68-70°C; FT-IR spectrum (KBr pellet): ν 3018 (w, arom. C-H), 1580, 1490 (s, arom. C=C), 1098 cm^{-1} ; $^1\text{H-NMR}$ spectrum (CDCl_3): δ 8.00- 7.90 (m, 4H), 7.50-7.30 (m, 5H), 2.63 (q, 2H, $J = 7.5$ Hz), 1.24 (t, 3H, $J = 7.5$ Hz) ppm; $^{13}\text{C-NMR}$ spectrum (CDCl_3): δ 159.1, 147.6, 143.0, 138.1, 129.2, 128.9, 128.5, 128.2, 127.0, 126.7, 125.2, 115.9, 115.5, 28.8, 15.5 ppm.

3.3.2 Preparation of 2-[4'-(1-bromoethyl)-phenyl]-4-chloro-5-phenyloxazole

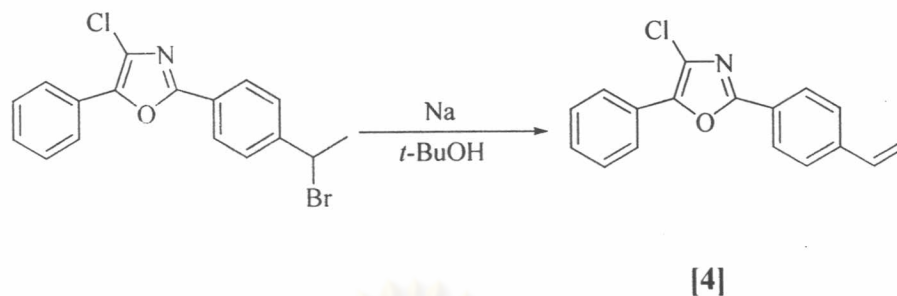


[3]

N-Bromosuccinimide (0.89 g, 5.0 mmol), 4-chloro-2-(4'-ethylphenyl)-5-phenyloxazole (1.42 g, 5.0 mmol), benzoyl peroxide (0.05 g, 0.2 mmol) and carbon tetrachloride (15 mL) were placed in a 25 mL round bottom flask equipped with a condenser and a calcium chloride drying tube. The mixture was heated under reflux for one hour. The reaction mixture became yellow and a white precipitate separated. Then, the mixture was allowed to cool to room temperature and the succinimide was removed by filtration. The filtrate was concentrated to dryness by evaporation under vacuum. The yellow crude product was recrystallized from ethyl acetate to give 2-[4'-(1-bromoethyl)-phenyl]-4-chloro-5-phenyloxazole as a yellow solid (1.30 g, 72 %): mp. 81-83°C; FT-IR spectrum (KBr pellet): ν 3032 (w, arom. C-H), 1581, 1490 (s, arom. C=C) cm^{-1} ; $^1\text{H-NMR}$ spectrum (CDCl_3): δ 8.05- 7.90 (m, 4H), 7.55-7.30 (m, 5H), 5.19 (q, 1H, $J = 7.0$ Hz), 2.04 (d, 3H, $J = 7.0$ Hz) ppm; $^{13}\text{C-NMR}$ spectrum (CDCl_3): δ 158.0, 145.8, 140.0, 132.8, 130.2, 129.2, 128.9, 128.5, 126.7, 125.2, 115.9, 115.5, 48.2, 26.4 ppm.

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3.3.3 Preparation of 4-chloro-5-phenyl-2-(4'-vinylphenyl)oxazole



Sodium *t*-butoxide was prepared in *t*-butanol. 2-[4'-(1-Bromoethyl)-phenyl]-4-chloro-5-phenyloxazole (0.72 g, 1 mmol) was added to the solution. The mixture was refluxed for three hours. After this time, the solution was cooled to room temperature and poured onto approximately 25 g of crush ice with continuous stirring. The cool mixture was extracted with methylene chloride and then dried over sodium sulfate anhydrous. The mixture was further purified by column chromatography using 30% ethyl acetate in hexane as an eluent. The yield of the yellow solid product was 0.21 g (10% yield); mp. 82-84°C; FT-IR spectrum (KBr pellet): ν 3016 (w, arom. C-H), 1581, 1494 (s, arom. C=C), 1278 (w, C-N) cm^{-1} ; $^1\text{H-NMR}$ spectrum (CDCl_3): δ 8.05-7.91 (m, 4H), 7.52-7.23 (m, 4H), 6.85-6.65 (m, 1H), 5.49-5.27 (m, 2H) ppm; $^{13}\text{C-NMR}$ spectrum (CDCl_3): δ 150.6, 146.7, 140.9, 139.8, 138.1, 135.4, 127.8, 127.2, 126.5, 121.4, 115.8.

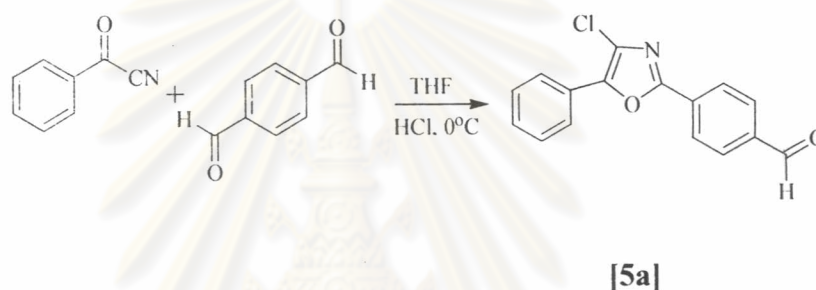
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3.4 Synthesis of [4-(4'-chloro-5'-phenyloxazol-2'-yl)phenyl]methyl methacrylate derivatives

The synthetic procedure of 4-(4'-chloro-5'-phenyloxazol-2'-yl)phenyl]methyl methacrylate derivatives is showed in the following three steps.

3.4.1 Preparation of 4-[4'-chloro-5'-(4-substituted phenyl)-oxazol-2'-yl]benzaldehyde

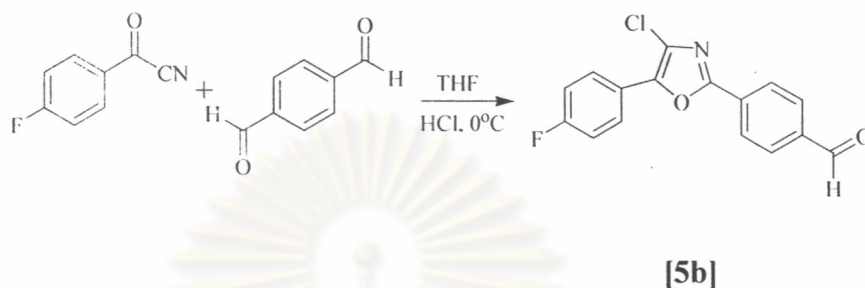
3.4.1.1 Synthesis of 4-(4'-chloro-5'-phenyl-oxazol-2'-yl)benzaldehyde



Benzoyl cyanide (2.38 g, 20 mmol) and terephthalaldehyde (2.68 g, 20 mmol) in 50 mL dry THF were contained in a reaction flask. The reaction flask was then connected to a HCl gas generator. The reaction mixture was allowed to cool in an ice-NaCl cooling bath to 0°C and then dry HCl gas passed into the solution flask until the HCl gas was no longer absorbed by the reaction mixture, tested by ammonia at the outlet of the reaction flask. At this stage, the reaction flask was quickly sealed and kept at 0°C for 2 days. The reaction mixture was then poured onto an ice with continuous stirring and subsequently filtered. The product was recrystallized from ethyl acetate to give 4-(4-chloro-5-phenyl-oxazol-2-yl)-benzaldehyde as a colorless solid (4.14 g, 73 %): mp.= 128-129°C; FT-IR spectrum (KBr pellet): ν 3055 (w, arom. C-H), 1704 (s, arom. C=O), 1581, 1488 (s, arom. C=C), 1098 (w, C-Cl) cm^{-1} ; $^1\text{H-NMR}$ spectrum (CDCl_3): δ 10.07 (m, 1H), 8.23- 8.22 (m, 2H), 8.02- 8.00 (m, 2H), 7.56- 7.52 (dd, 2H, $J = 7.0$ Hz), 7.46- 7.44 (m, 2H) ppm; $^{13}\text{C-NMR}$ spectrum (CDCl_3): δ 171.0, 133.8, 133.0, 132.8, 130.2, 129.2, 128.9, 128.5, 126.7, 125.2, 115.9, 115.5 ppm; UV (THF): $\lambda_{\text{max}} = 351$ nm, $\log \epsilon_{\text{max}} = 4.45$; Fluorescence emission (THF):

$\lambda_{\max} = 426 \text{ nm}$; MS m/z : 284 M^+ , 286 $(M+2)^+$ a third as large as M^+ ; Anal. Calcd for $C_{16}H_{10}ClNO_2$: C, 67.74; H, 3.55; N, 4.94. Found: C, 67.33; H, 3.51; N, 4.94.

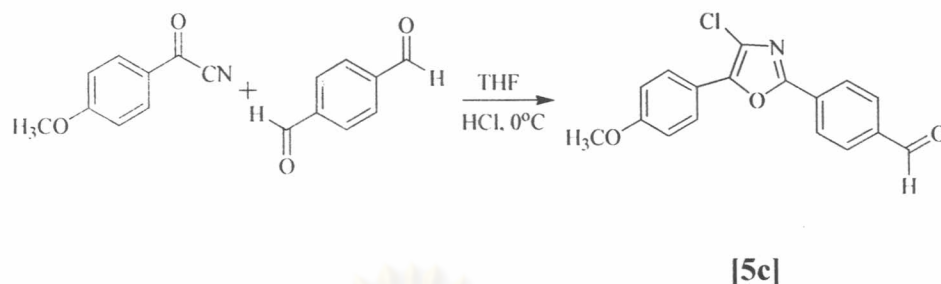
3.4.1.2 Synthesis of 4-[4'-chloro-5'-(4-fluorophenyl)oxazol-2'-yl]benzaldehyde



By using the same procedure as described for **[5a]**, 4-fluorobenzoyl cyanide (2.98 g, 20 mmol) was used instead of benzoyl cyanide. The product was obtained as a light yellow solid (3.62 g, 60 %): mp. 142-143°C; FT-IR spectrum (KBr pellet): ν 2818, 2731 (w, CHO), 1699 (s, arom. C=O), 1606, 1493 (s, arom. C=C), 1237 (w, C-F), 1088 (w, C-Cl) cm^{-1} ; $^1\text{H-NMR}$ spectrum (CDCl_3): δ 10.12 (s, 1H), 8.28- 8.26 (dd, 2H; $J = 8.0 \text{ Hz}$), 8.05- 8.03 (dd, 2H, $J = 9.0 \text{ Hz}$), 8.01- 7.98 (dd, 2H, $J = 6.0 \text{ Hz}$), 7.26- 7.22 (dd, 2H, $J = 9.0 \text{ Hz}$) ppm; $^{13}\text{C-NMR}$ spectrum (CDCl_3): δ 191.5, 171.1, 168.9, 163.8, 161.1, 133.0, 132.8, 130.1, 125.5, 115.9, 115.5 ppm; UV (THF): $\lambda_{\max} = 346 \text{ nm}$, $\log \epsilon_{\max} = 4.29$; Fluorescence emission (THF): $\lambda_{\max} = 430 \text{ nm}$; MS m/z : 301 M^+ , 303 $(M+2)^+$ a third as large as M^+ ; Anal. Calcd for $C_{16}H_9ClFNO_2$: C, 63.70; H, 3.01; N, 4.64. Found: C, 63.53; H, 3.12; N, 4.60.

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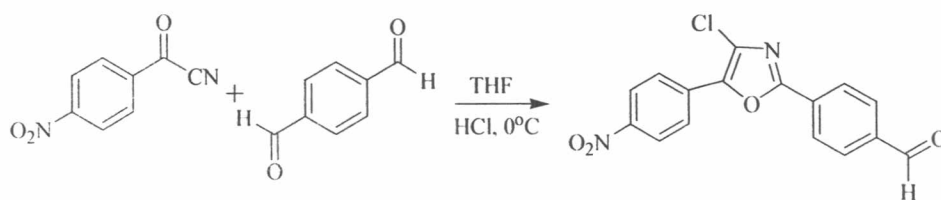
3.4.1.3 Synthesis of 4-[4'-chloro-5'-(4-methoxyphenyl)oxazol-2'-yl]benzaldehyde



By using the same procedure as described for **[5a]**, 4-methoxybenzoyl cyanide (3.22 g, 20 mmol) was used instead of benzoyl cyanide. The product was obtained as a light yellow solid (3.14 g, 50 %yield): mp. 138-140°C; FT-IR spectrum (KBr pellet): ν 2834 (w, CHO), 1699 (s, arom.C=O), 1606, 1504 (s, arom. C=C), 1257 (w, C-O), 1175 (w, C-Cl) cm^{-1} ; $^1\text{H-NMR}$ spectrum (CDCl_3): δ 10.10 (s, 1H), 8.26- 8.24 (dd, 2H, $J = 8.0$ Hz), 8.03- 8.01 (dd, 2H, $J = 8.0$ Hz), 7.94- 7.92 (dd, 2H, $J = 8.0$ Hz), 7.07- 7.05 (dd, 2H, $J = 8.0$ Hz) ppm; $^{13}\text{C-NMR}$ spectrum (CDCl_3): δ 191.4, 171.4, 164.0, 160.2, 137.3, 132.3, 131.5, 131.4, 130.2, 126.9, 126.5, 119.1, 114.4, 113.7, 55.4; UV (THF): $\lambda_{\text{max}} = 360$ nm, $\log \epsilon_{\text{max}} = 4.61$; Fluorescence emission (THF): $\lambda_{\text{max}} = 462$ nm; MS m/z : 313 M^+ , 315 ($\text{M} + 2$) $^+$ a third as large as M^+ ; Anal. Calcd for $\text{C}_{17}\text{H}_{12}\text{ClNO}_3$: C, 65.08; H, 3.86; N, 4.46. Found: C, 65.01; H, 3.96; N, 4.53.

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3.4.1.4 Synthesis of 4-[4'-chloro-5'-(4-nitrophenyl)oxazol-2'-yl]benzaldehyde



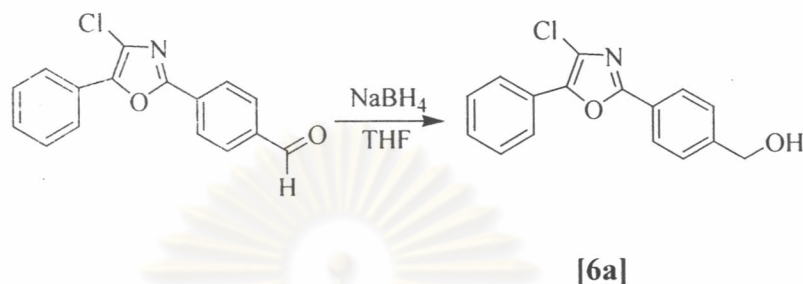
[5d]

By using the same procedure as described for [5a], 4-nitrobenzoyl cyanide (3.52 g, 20 mmol) was used instead of benzoyl cyanide. The product was obtained as a yellow solid (4.93 g, 75 %): mp. 218-220°C.; FT-IR spectrum (KBr pellet): ν 3106 (w, arom. C-H), 1704 (s, arom. C=O), 1691, 1514 (s, arom. C=C), 1339 (m, C-N), 1103 (w, C-Cl) cm^{-1} ; $^1\text{H-NMR}$ spectrum (DMSO): δ 10.15 (s, 1H), 8.42- 8.40 (dd, 2H, $J = 8.0$ Hz), 8.33- 8.31 (dd, 2H, $J = 8.0$ Hz), 8.20- 8.18 (dd, 2H, $J = 8.0$ Hz), 8.18-8.09 (dd, 2H, $J = 8.0$ Hz) ppm; $^{13}\text{C-NMR}$ spectrum (DMSO): δ 190.4, 150.6, 148.4, 142.6, 142.3, 138.1, 136.7, 130.2, 127.9, 127.5, 125.4, 124.1; UV (THF): $\lambda_{\text{max}} = 363$ nm, $\log \epsilon_{\text{max}} = 4.37$; Fluorescence emission (THF): $\lambda_{\text{max}} = 426$ nm; MS m/z : 328 M^+ , 330 $(M+2)^+$ a third as large as M^+ ; Anal. Calcd for $\text{C}_{16}\text{H}_9\text{ClN}_2\text{O}_4$: C, 58.46; H, 2.76; N, 8.52. Found: C, 58.29; H, 2.95; N, 8.46.

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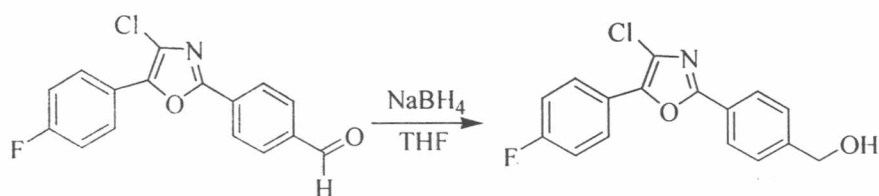
3.4.2 Preparation of [4-(4'-chloro-5'-phenyl-oxazol-2'-yl)-phenyl]methanol derivatives

3.4.2.1 Synthesis of [4-(4'-chloro-5'-phenyl-oxazol-2'-yl)-phenyl]methanol



4-(4'-Chloro-5'-phenyl-oxazol-2'-yl)-benzaldehyde (2.84 g, 10 mmol), sodium borohydride (0.2 g, 4 mmol) and THF 50 ml were placed in Erlenmeyer flask and stirred vigorously for 3 hours at room temperature. Then water (15 ml) was added and heated the aqueous THF solution just to boiling point. After this time, the solution was allowed to cool to room temperature and poured into ice water. The precipitate was filtered and recrystallized from hexane/ethyl acetate to give [4-(4'-chloro-5'-phenyl-oxazol-2'-yl)-phenyl]-methanol as a colorless solid (2.43 g, 85 %): mp. 132-133°C; FT-IR spectrum (KBr pellet): ν 3342 (b, O-H), 3049 (w, arom. C-H), 1581, 1493 (s, arom. C=C), 1206 (s, C-O) cm^{-1} ; $^1\text{H-NMR}$ spectrum (CDCl_3): δ 8.11- 8.09 (dd, 2H, $J = 8.0$ Hz), 7.99- 7.97 (dd, 2H, $J = 8.0$ Hz), 7.54- 7.51 (dd, 3H, $J = 8.0$ Hz), 7.44- 7.40 (dd, 2H, $J = 7.5$ Hz), 4.81 (s, 2H), 1.84 (b, 1H) ppm; $^{13}\text{C-NMR}$ spectrum (CDCl_3): δ 150.6, 140.9, 138.1, 135.4, 136.1, 129.0, 128.5, 127.8, 127.2, 127.0, 68.5; UV (THF): $\lambda_{\text{max}} = 311$ nm, $\log \epsilon_{\text{max}} = 4.56$; Fluorescence emission (THF): $\lambda_{\text{max}} = 370$ nm; MS m/z : 286 M^+ , 288 $(\text{M} + 2)^+$ a third as large as M^+ ; Anal. Calcd for $\text{C}_{16}\text{H}_{12}\text{ClNO}_2$: C, 67.26; H, 4.23; N, 4.90. Found: C, 67.24; H, 4.17; N, 4.96.

3.4.2.2 Synthesis of {4-[4'-chloro-5'-(4-fluorophenyl)oxazol-2'-yl]phenyl} methanol

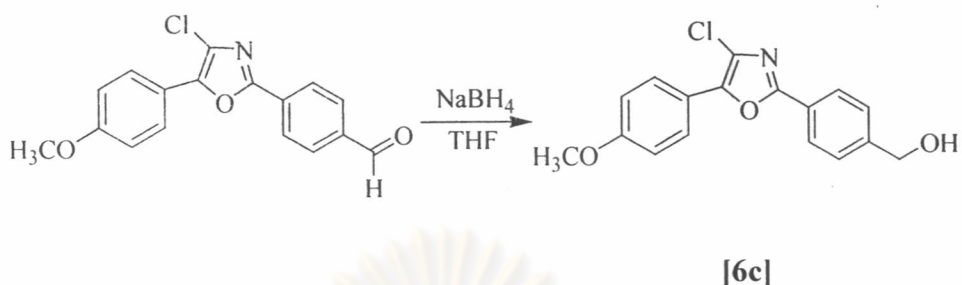


[6b]

By using the same procedure as described for the preparation of [6a], 4-[4'-chloro-5'-(4-fluorophenyl)-oxazol-2'-yl]-benzaldehyde (3.01 g, 10 mmol) was used instead of 4-(4'-chloro-5'-phenyloxazol-2'-yl)-benzaldehyde. The product was obtained as a yellow solid (2.42 g, 80 %): mp. 132-134°C; FT-IR spectrum (KBr pellet): ν 3316 (b, O-H), 2870 (w, arom. C-H), 1576, 1499 (s, arom. C=C) 1237 (w, C-F) cm^{-1} ; $^1\text{H-NMR}$ spectrum (CDCl_3): δ 8.10- 8.08 (dd, 2H, $J = 8.0$ Hz), 7.98- 7.95 (dd, 2H, $J = 8.0$ Hz), 7.53- 7.51 (dd, 2H, $J = 8.0$ Hz), 7.23- 7.19 (dd, 2H, $J = 8.0$ Hz), 4.81 (s, 2H), 2.08 (b, 1H) ppm; $^{13}\text{C-NMR}$ spectrum (CDCl_3): δ 162.1, 150.6, 140.9, 138.1, 135.4, 132.1, 128.6, 127.8, 127.2, 125.4, 116.0, 68.5; UV (THF): $\lambda_{\text{max}} = 311$ nm, $\log \epsilon_{\text{max}} = 4.47$; Fluorescence emission (THF): $\lambda_{\text{max}} = 371$ nm ; MS m/z : 303 M^+ , 305 ($\text{M} + 2$) $^+$ a third as large as M^+ ; Anal. Calcd for $\text{C}_{16}\text{H}_{11}\text{ClFNO}_2$: C, 63.27; H, 3.65; N, 4.61. Found: C, 63.33; H, 3.61; N, 4.64.

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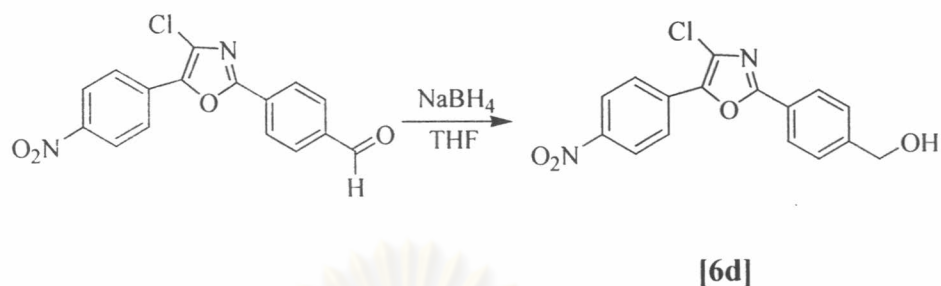
3.4.2.3 Synthesis of {4-[4'-chloro-5'-(4-methoxyphenyl)oxazol-2'-yl]phenyl} methanol



By using the same procedure as described for the preparation of **[6a]**, 4-[4'-chloro-5'-(4-methoxyphenyl)-oxazol-2'-yl]-benzaldehyde (3.13 g, 10 mmol) was used instead of 4-(4'-chloro-5'-phenyloxazol-2'-yl)-benzaldehyde. The product was obtained as a yellow solid (2.68 g, 85 %): mp. 146-148°C; FT-IR spectrum (KBr pellet): 3358 (b, O-H), 2916 (w, arom. C-H), 1611, 1504 (s, arom. C=C), 1252 (w, C-O), 1031 (w, C-Cl) cm^{-1} ; $^1\text{H-NMR}$ spectrum (CDCl_3): δ 8.10- 8.08 (dd, 2H, $J = 8.0$ Hz), 7.93- 7.91 (dd, 2H, $J = 9.0$ Hz), 7.53- 7.51 (dd, 2H, $J = 8.0$ Hz), 7.06-7.04 (dd, 2H; $J = 9.0$ Hz), 4.81 (s, 2H), 3.91 (s, 3H), 1.646 (b, 1H) ppm; $^{13}\text{C-NMR}$ spectrum (CDCl_3): δ 162.0, 150.6, 140.9, 138.1, 135.4, 128.8, 128.0, 127.8, 127.2, 114.6, 68.5, 56.0; UV (THF): $\lambda_{\text{max}} = 321$ nm, $\log \epsilon_{\text{max}} = 4.66$; Fluorescence emission (THF): $\lambda_{\text{max}} = 393$ nm ; MS m/z : 315 M^+ , 317 ($\text{M} + 2$) $^+$ a third as large as M^+ ; Anal. Calcd for $\text{C}_{17}\text{H}_{14}\text{ClNO}_3$: C, 64.67; H, 4.47; N, 4.44. Found: C, 64.31; H, 4.33; N, 4.55.

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3.4.2.4 Synthesis of {4-[4'-chloro-5'-(4-nitrophenyl)oxazol-2'-yl]phenyl} methanol

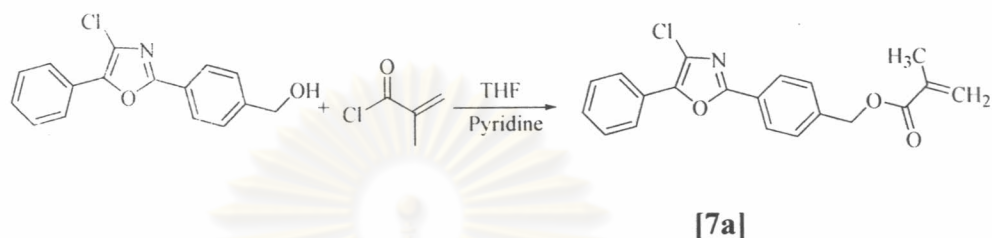


By using the same procedure as described for [6a], 4-[4'-chloro-5'-(4-nitrophenyl)-oxazol-2'-yl]-benzaldehyde (3.28 g, 10 mmol) was used instead of 4-(4'-chloro-5'-phenyloxazol-2'-yl)-benzaldehyde. The product was obtained as a yellow solid (2.48 g, 75 %): mp. 192-193°C; FT-IR spectrum (KBr pellet): 3286 (b, O-H), 2865 (w, arom. C-H), 1596, 1509 (s, arom. C=C), 1334 (w, C-N), 1216 (w, C-O), 1036 (w, C-Cl) cm⁻¹; ¹H-NMR spectrum (DMSO): δ 8.39- 8.36 (dd, 2H, *J* = 8.0 Hz), 8.17- 8.12 (dd, 4H, *J* = 9.0 Hz), 7.57- 7.55 (dd, 2H, *J* = 8.0 Hz), 4.84 (s, 2H), 1.96 (b, 1H) ppm; ¹³C-NMR spectrum (DMSO): δ 150.6, 148.4, 142.6, 140.9, 138.1, 127.8, 127.9, 127.2, 125.4, 68.5; UV (THF): λ_{max} = 358 nm, log ε_{max} = 4.44; Fluorescence emission (THF): λ_{max} = 402 nm; MS *m/z*: 330 M⁺, 332 (M+2)⁺ a third as large as M⁺; Anal. Calcd for C₁₆H₁₁ClN₂O₄: C, 58.11; H, 3.35; N, 8.47. Found: C, 58.60; H, 3.47; N, 8.47.

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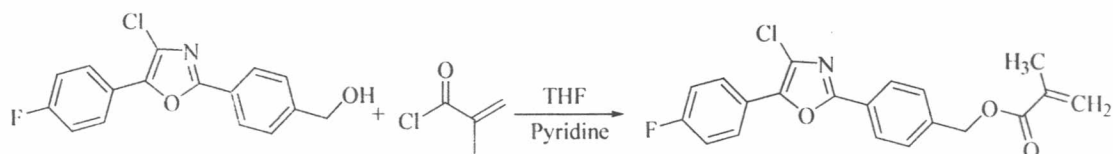
3.4.3 Preparation of 4-[4'-chloro-5'-(4-substituted phenyl)oxazol-2'-yl]phenyl]methyl methacrylate

3.4.3.1 Synthesis of 4-(4'-chloro-5'-phenyloxazol-2'-yl)phenyl]methyl methacrylate



To a 100 ml three-neck round bottom flask equipped with a condenser, a nitrogen inlet and a rubber stopper was charged with [4-(4'-chloro-5'-phenyloxazol-2'-yl)-phenyl]methanol (1.48 g, 5 mmol) and 15 mL of THF. Dry pyridine (0.6 ml, 75 mmol) was slowly added to the reaction flask. Just at the beginning of the reaction, an ice bath was used to control the medium temperature. Then methyl methacryloyl chloride (0.53 mL, 55 mmol) was slowly introduced to the reaction flask and stirred for 24 hours. At the end of the reaction, ground ice was added. The insoluble samples were recovered by filtration and washed with cold water and methanol. The product was further purified by flash chromatography using 30% ethyl acetate in hexane as an eluent. The yield of the white solid product was 0.88 g, 50 %, mp. 72-73°C. FT-IR spectrum (KBr pellet): ν 3049 (w, arom. C-H), 1724 (s, arom. C=O), 1499, 1329 (s, arom. C=C), 1190 (w, C-Cl) cm^{-1} ; $^1\text{H-NMR}$ spectrum (CDCl_3): δ 8.14- 8.12 (dd, 2H, $J = 8.0$ Hz), 8.00- 7.98 (dd, 2H, $J = 8.0$ Hz), 7.54- 7.53 (dd, 4H, $J = 6.0$ Hz), 7.45- 7.43 (dd, 1H, $J = 7.0$ Hz), 6.23 (s, 1H), 5.67 (s, 1H), 5.29 (s, 2H), 2.03 (s, 3H) ppm; $^{13}\text{C-NMR}$ spectrum (CDCl_3): δ 165.0, 150.6, 140.9, 138.1, 136.5, 135.4, 129.0, 128.5, 127.8, 127.2, 127.0, 121.4, 72.6, 18.4; UV (THF): $\lambda_{\text{max}} = 311$ nm, $\log \epsilon_{\text{max}} = 4.49$; Fluorescence emission (THF): $\lambda_{\text{max}} = 375$ nm ; MS m/z : 354 M^+ , 356 ($\text{M} + 2$) $^+$ a third as large as M^+ ; Anal. Calcd for $\text{C}_{20}\text{H}_{16}\text{ClNO}_3$: C, 67.90; H, 4.56; N, 3.96. Found: C, 67.91; H, 4.53; N, 3.94.

3.4.3.2 Synthesis of {4-[4'-chloro-5'-(4-fluorophenyl)oxazol-2'-yl]phenyl} methyl methacrylate

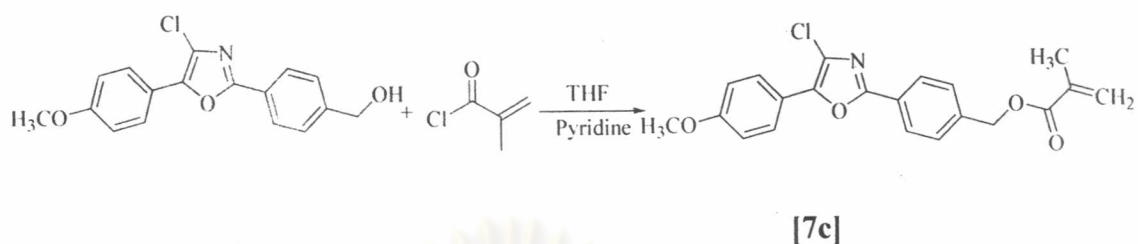


[7b]

By using the same procedure as described for [7a], {4-[4'-chloro-5'-(4-fluorophenyl)oxazol-2'-yl]-phenyl}methanol (1.52 g, 5 mmol) was used instead of [4-(4'-chloro-5'-phenyloxazol-2'-yl)-phenyl]methanol. The product was obtained as a yellow solid (1.02 g, 55 %): mp. 106-108°C; FT-R spectrum (KBr pellet): ν 3070 (w, arom. C-H), 1785 (s, arom. C=O), 1581, 1499 (s, arom. C=C), 1293 (C-F), 1154 (w, C-O), 1088 (w, C-Cl) cm^{-1} ; $^1\text{H-NMR}$ spectrum (CDCl_3): δ 8.11- 8.09 (dd, 2H, $J = 8.0$ Hz), 7.98- 7.94 (dd, 2H, $J = 9.0$ Hz), 7.53- 7.51 (dd, 2H, $J = 8.0$ Hz), 7.24- 7.20 (dd, 2H, $J = 9.0$ Hz), 6.23 (s, 1H), 5.66 (s, 1H), 5.28 (s, 2H), 2.03 (s, 3H) ppm; $^{13}\text{C-NMR}$ spectrum (CDCl_3): δ 165.0, 162.1, 150.6, 140.9, 139.8, 138.1, 135.4, 135.4, 128.6, 127.8, 127.2, 125.4, 116.0, 72.6, 18.4; UV (THF): $\lambda_{\text{max}} = 311$ nm, $\log \epsilon_{\text{max}} = 4.46$; Fluorescence emission (THF): $\lambda_{\text{max}} = 377$ nm; MS m/z : 372 M^+ , 374 $(\text{M} + 2)^+$ a third as large as M^+ ; Anal. Calcd for $\text{C}_{20}\text{H}_{15}\text{ClFNO}_3$: C, 64.61; H, 4.07; N, 3.77. Found: C, 64.67; H, 4.11; N, 3.74.

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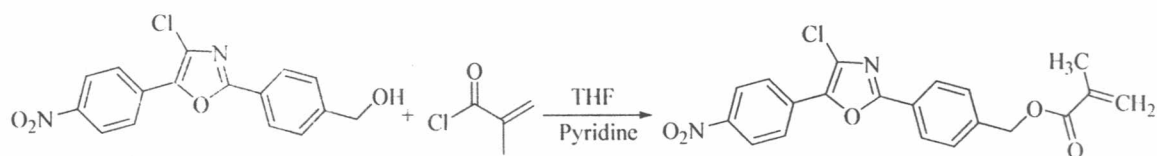
3.4.3.3 Synthesis of {4-[4'-chloro-5'-(4-methoxyphenyl)oxazol-2'-yl]phenyl} methyl methacrylate



By using the same procedure as described for **[7a]**, {4-[4'-chloro-5'-(4-methoxyphenyl)-oxazol-2'-yl]-phenyl}methanol (1.58 g, 5 mmol) was used instead of [4-(4'-chloro-5'-phenyloxazol-2'-yl)-phenyl]methanol. The product was obtained as a yellow solid (1.15 g, 60 %): mp. 100-102°C; FT-IR spectrum (KBr pellet): 2936 (w, arom. C-H), 1719 (s, arom. C=O), 1611, 1504 (s, arom. C=C), 1257 (w, C-O), 1031 (w, C-Cl) cm^{-1} ; $^1\text{H-NMR}$ spectrum (CDCl_3): δ 8.10- 8.08 (dd, 2H, $J = 8.0$ Hz), 7.93- 7.90 (dd, 2H, $J = 8.0$ Hz), 7.53- 7.51 (dd, 2H, $J = 8.0$ Hz), 7.06- 7.04 (dd, 2H, $J = 8.0$ Hz), 6.23 (s, 1H), 5.66 (s, 1H), 5.28 (s, 2H), 3.91 (s, 3H), 2.03 (s, 3H) ppm; $^{13}\text{C-NMR}$ spectrum (CDCl_3): δ 165.0, 162.0, 150.6, 148.4, 140.9, 139.8, 138.1, 135.4, 127.9, 127.8, 127.2, 125.4, 124.1, 72.6, 56.0, 18.4; UV (THF): $\lambda_{\text{max}} = 324$ nm, $\log \epsilon_{\text{max}} = 4.47$; Fluorescence emission (THF): $\lambda_{\text{max}} = 400$ nm; MS m/z : 383 M^+ , 385 ($\text{M} + 2$) $^+$ a third as large as M^+ ; Anal. Calcd for $\text{C}_{21}\text{H}_{18}\text{ClNO}_4$: C, 65.71; H, 4.73; N, 3.65. Found: C, 65.41; H, 4.51; N, 3.43.

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3.4.3.4 Synthesis of {4-[4'-chloro-5'-(4-nitrophenyl)oxazol-2'-yl]phenyl} methyl methacrylate

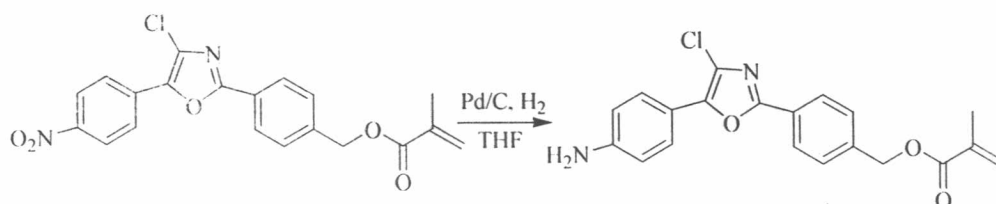


[7d]

By using the same procedure as described for [7a], {4-[4'-chloro-5'-(4-nitrophenyl)-oxazol-2'-yl]-phenyl}methanol (1.65 g, 5 mmol) was used instead of [4-(4'-chloro-5'-phenyloxazol-2'-yl)-phenyl]methanol. The product was obtained as a yellow solid (1.00 g, 50 %): mp. 120-122°C; FT-IR spectrum (KBr pellet): ν 3101 (w, arom. C-H), 1714 (s, arom. C=O), 1691, 1519 (s, arom. C=C), 1334 (w, C-N), 1154 (m, C-O), 1108 (m, C-Cl) cm^{-1} ; $^1\text{H-NMR}$ spectrum (DMSO): δ 8.40- 8.38 (dd, 2H, $J = 8.0$ Hz), 8.18- 8.13 (m, 4H), 7.57- 7.53 (dd, 2H arom., $J = 8.0$ Hz), 6.24 (s, 1H), 5.68 (s, 1H), 5.31 (s, 2H), 2.08 (s, 3H) ppm; $^{13}\text{C-NMR}$ spectrum (DMSO): δ 165.0, 162.0, 150.6, 148.4, 140.9, 139.8, 138.1, 135.4, 127.9, 127.8, 127.2, 125.4, 124.1, 72.6, 18.4; UV (THF): $\lambda_{\text{max}} = 356$ nm, $\log \epsilon_{\text{max}} = 4.46$; Fluorescence emission (THF): $\lambda_{\text{max}} = 425$ nm; MS m/z : 398 M^+ , 400 $(\text{M} + 2)^+$ a third as large as M^+ ; Anal. Calcd for $\text{C}_{20}\text{H}_{15}\text{ClN}_2\text{O}_5$: C, 60.23; H, 3.79; N, 7.02. Found: C, 58.58; H, 3.89; N, 7.08.

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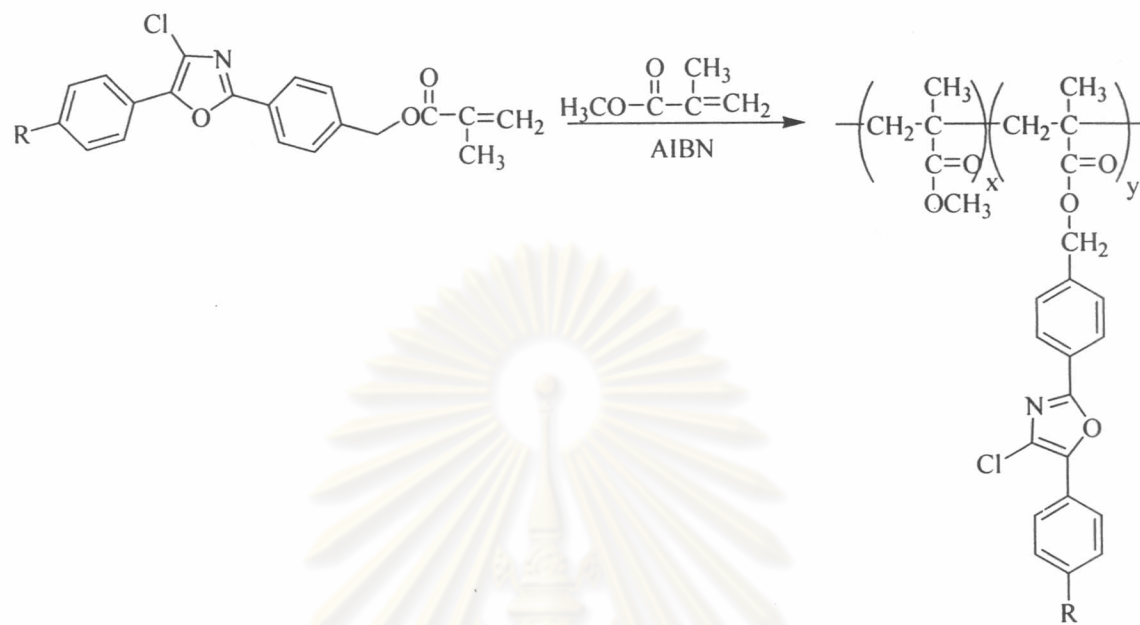
3.4.3.5 Synthesis of {4-[4'-chloro-5'-(4-aminophenyl)oxazol-2'-yl]phenyl} methyl methacrylate



[7e]

To a Parr bottle were added {4-[4'-chloro-5'-(4-nitrophenyl)oxazol-2'-yl]phenyl} methyl methacrylate (2.5 g, 6 mmol), dry THF 10 mL and a 5% Pd/C (0.01 mmol). The bottle was placed in a shaker type hydrogenation apparatus and agitated under hydrogen (65-55 psi) at room temperature for 10 mins. The mixture was filtered through Celite, and the residue rinsed with THF until the rinse was no longer colored. The filtrate was evaporated to dryness under reduced pressure. The product was further purified by flash chromatography (hexane/ethyl acetate = 7/3). The yield of the yellow solid product was 0.88 g (40% yield); mp. 122-124°C; FT-IR spectrum (KBr pellet): ν 3368 (m, N-H), 2921 (w, arom. C-H), 1730 (s, arom. C=O), 1611, 1504 (s, arom. C=C), 1293 (w, C-N), 1149 (m, C-O) cm^{-1} ; $^1\text{H-NMR}$ spectrum (DMSO): δ 7.85- 7.75 (dd, 2H, $J = 8.0$ Hz), 7.68- 7.40 (m, 4H), 6.84-6.75 (dd, 2H arom., $J = 8.0$ Hz), 6.25 (s, 1H), 5.69 (s, 1H), 5.22 (s, 2H), 4.05-3.90 (b, 2H), 1.90 (s, 3H) ppm; $^{13}\text{C-NMR}$ spectrum (DMSO): δ 165.6, 150.7, 146.9, 139.8, 138.1, 135.4, 128.9, 127.6, 126.8, 121.4, 73.1, 18.6; UV (THF): $\lambda_{\text{max}} = 352$ nm, $\log \epsilon_{\text{max}} = 4.21$; Fluorescence emission (THF): $\lambda_{\text{max}} = 456$ nm; MS m/z : 368 M^+ , 370 ($\text{M} + 2$) $^+$ a third as large as M^+ ; Anal. Calcd for $\text{C}_{20}\text{H}_{17}\text{ClN}_2\text{O}_3$: C, 65.13; H, 4.65; N, 7.60. Found: C, 65.08; H, 4.70; N, 7.63.

3.5 Free-radical polymerization



26.1 mg of the acrylate monomer, 0.73 g of MMA and 12.5 mg (1 mol% to the total monomer) of 2,2'-azobisisobutyronitrile (AIBN) were dissolved in 5 mL of THF. The solution was thoroughly degassed by several freeze-pump-thaw cycles and heated in a sealed ampoule at 60 °C for 48 h. The solution was cooled and slowly poured with vigorous stirring into methanol to precipitate the polymer. After filtering, the product was washed with methanol and dried in a vacuum oven.

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Table 3.1: Feed ratio for the preparation of polymers

Polymer	Substituents (R)	Feed Ratio (Mole %)
		Fluorescent monomer/MMA
[P ₁]	R = H	1/99
[P ₅]		5/95
[Pf1]	R = F	1/99
[Pf5]		5/95
[Pm1]	R = OCH ₃	1/99
[Pm5]		5/95
[Pn1]	R = NO ₂	1/99
[Pn5]		5/95
[Pnh2]	R = NH ₂	5/95

3.6 Characterization of free-radical polymers

3.6.1 Determination of molecular weight

The molecular weights of the polymers used in this work were determined using gel permeation chromatography (GPC). A UV detector was used to provide data that was analyzed to determine the molecular weights of the polymer materials. Samples were prepared as solution of 0.1 wt% in THF. Monodisperse polystyrene standards were used for calibration of the molecular weights. Number average molecular weight (M_n), weight average molecular weight (M_w), and polydispersity index (PDI) were calculated for each sample from the output of the UV detector

3.6.2. Determination of Thermal Properties

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were used to determine the approximate glass transition temperature (T_g) and decomposition temperature (T_d) of the polymer samples. To determine T_g , two lines are drawn parallel to the baseline above and below the inflection at T_g . The midpoint

of the departure from the left and the intersection with the baseline nearest T_g on the right is determined by the instrument. This midpoint is taken as the glass transition temperature. T_d was determined at 5% weight losses.

3.6.3 Polymer solubility

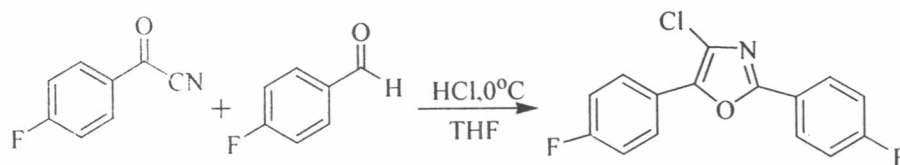
The samples were dispersed in the solvents at concentration in the range 5-20 g/L. The dispersions were maintained under stirring overnight at room temperature. The solubility was determined by the residual mass after centrifugation.



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Part B: Preparation of condensation polymers

3.7 Synthesis of 4-chloro-2,5-bis-(4'-fluorophenyl)oxazole



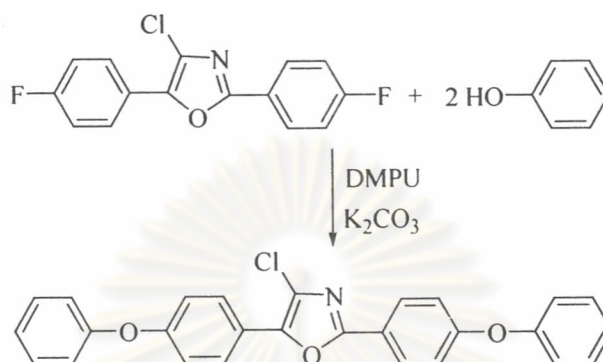
[8]

By using the same procedure as described for [5a], 4-fluorobenzoyl cyanide (25 mmol, 3.72g) and 4-fluorobenzaldehyde (20 mmol, 3.10 g) were used instead of benzoyl cyanide and terephthalaldehyde, respectively. The product was obtained as a white crystals (2.36 g, 44%): mp 110-112°C; FT-IR spectrum (KBr pellet): ν 3080 (w, arom. C-H), 1606, 1499 (s, arom. C=C), 1226 (m, C-F), 1083 (m, C-Cl) cm^{-1} ; $^1\text{H-NMR}$ spectrum (CDCl_3): δ 8.12- 8.08 (dd, 2H, $J = 8.0$ Hz), 7.97- 7.93 (dd, 2H, $J = 8.0$ Hz), 7.24- 7.19 (dd, 4H, $J = 8.0$ Hz) ppm; $^{13}\text{C-NMR}$ spectrum (CDCl_3): δ 171.0, 168.9, 163.8, 132.9, 132.7, 125.9, 115.9, 115.5; UV (THF): $\lambda_{\text{max}} = 264$ nm, $\log \epsilon_{\text{max}} = 4.20$; Fluorescence emission (THF): $\lambda_{\text{max}} = 369$ nm ; Anal. Calcd for $\text{C}_{16}\text{H}_{10}\text{ClNO}_2$: C, 61.77; H, 2.76; N, 4.08. Found: C, 61.05; H, 2.78; N, 4.91.

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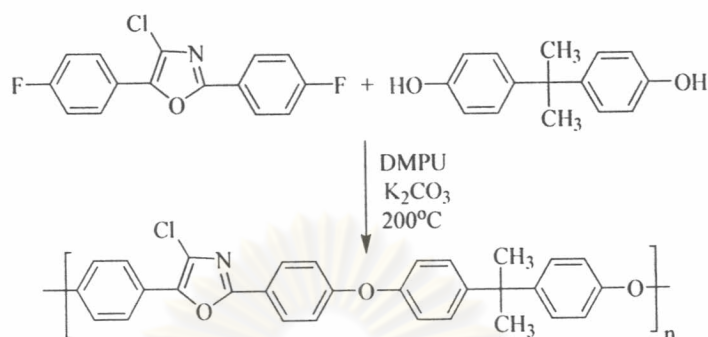
3.8 Condensation polymerization

3.8.1 Model reaction



Oxazole monomer (0.73 g, 2.5 mmol) and phenol (0.46 g, 5.0 mmol) were dissolved in 20 mL of DMPU and 10 mL of toluene under nitrogen in a round-bottom flask with a reflux condenser, a nitrogen inlet, and a Dean-Stark trap. Potassium carbonate was added (0.75 g, 5.1 mmol), and the mixture was refluxed for 3 h at 180 °C in an oil bath. During refluxing, fresh and dry toluene was refilled twice. Finally, the temperature was raised to 220 °C while the toluene was removed through the Dean-Stark trap. The reaction was carried out for 3 h. At the end of reaction, 1 mL of acetic acid was added to neutralize the phenoxide, and the mixture was filtered while hot to remove salts. After the reaction was cooled to ambient temperature the product was precipitated by pouring the mixture into a mixture of 450 mL of methanol and 50 mL of water. The product was filtered off, washed several times with hot water and methanol and dried under reduced pressure. The yield of the brown solid product was 1.08 g (98%). FT-IR spectrum (KBr pellet): ν 3052 (w, arom. C-H), 1623 (s, arom. C=C), 1250 (C-O) cm^{-1} ; $^1\text{H-NMR}$ spectrum (CDCl_3): δ 7.46-7.22 (m, 8H arom.), 7.03-6.93 (m, 10H arom.) ppm.

3.8.2 Polymerization



Oxazole monomer (0.73 g, 2.5 mmol) and bisphenol A (0.57 g, 2.5 mmol) were dissolved in 20 mL of DMPU and 10 mL of toluene under nitrogen in a round-bottom flask with a reflux condenser, a nitrogen inlet, and a Dean-Stark trap. Potassium carbonate was added (0.75 g, 5.1 mmol), and the mixture was refluxed for 3 h at 180 °C in an oil bath temperature. During refluxing, fresh and dry toluene was refilled twice. Finally, the temperature was raised to 220 °C while the toluene was removed through the Dean-Stark trap. The reaction was carried out for 3, 6, 9 and 12 h. At the end of reaction, 1 mL of acetic acid was added to neutralize the phenoxide, and the mixture was filtered hot to remove salts. After the reaction was cooled to ambient temperature the polymer was coagulated in excess methanol. This product was filtered off, washed several times with hot water to remove any inorganic impurities, dried in vacuum. Then obtained polymer was dissolved in THF and the concentrated solution was reprecipitated in an excess of methanol. FT-IR spectrum (KBr pellet): ν 3072 (w, arom. C-H), 1608 (s, arom. C=O), 1512 (s, arom. C=C), 1250 (C-O) cm⁻¹; ¹H-NMR spectrum (CDCl₃): δ 8.19 (m, 2H arom., $J = 8.0$), 7.08 (m, 2H arom., $J = 8.0$) ppm.

3.9 Characterization of condensation polymers

3.9.1 Determination of molecular weight

The molecular weights of the condensation polymers at different reaction time, 3, 6, 9 and 12 h. were determined using GPC. A UV detector was used to provide data that was analyzed to determine the molecular weights of the polymer materials. Samples were prepared as solution of 0.1 wt% in THF.

3.9.2. Determination of thermal properties

DSC and TGA were used to determine the approximate T_g and T_d of the condensation polymers at different reaction time, 3, 6, 9 and 12 h. To determine T_g , two lines are drawn parallel to the baseline above and below the inflection at T_g . The midpoint of the departure from the left and the intersection with the baseline nearest T_g on the right is determined by the instrument. This midpoint is taken as the glass transition temperature. T_d was determined at 5% weight losses.

3.6.3 Polymer solubility

The condensation polymers at different reaction time, 3, 6, 9 and 12 h were dispersed in the solvents at concentration in the range 5-20 g/L. The dispersions were maintained under stirring overnight at room temperature. The solubility was determined by the residual mass after centrifugation.

Part C: Optical properties

3.10 UV absorption and fluorescence emission analysis

All UV absorption spectra were recorded at wavelengths between 200-500 nm at room temperature (25°C) with air-saturated solutions. The fluorescence emission were recorded at wavelength between 300-600 nm. 1 cm Pathlength quartz cuvettes were used for both UV and emission spectra. For solid state studies, thin films of copolymer were deposited on quartz slide.

3.11 Cyclic voltammetry

Voltammetric investigations of acrylic polymer and poly(aryl ether) oxazole were preformed in a three-electrod cell system with Ag/Ag⁺ reference in acetonitrile solutions containing 0.1 M of tetrabutyl ammonium tetra-fluoroborate (TBABF₄) as the supporting electrolyte. The polymer films dip-coated on carbon black electrodes were used as working electrodes and separately scanned anodically and cathodically.

3.12 Fabrication and characterization of LEDs

The single-layer LEDs was fabricated as sandwich structures between aluminum (Al) cathodes and indium-tin oxide (ITO) anodes. ITO-coated glass substrates were cleaned sequentially in ultrasonic bathes of detergent, toluene, deionized water and acetone. The polymer film was prepared by spin casting from the solution in chloroform (7mg/mL, 1500 rpm) followed by drying at 100°C. Finally, Al cathodes were thermally evaporated through a shadow mask onto the polymer films. Current-voltage characteristics of the LEDs were measured and carried out in ambient air under dc bias. All the device fabrication and characterization steps were done under ambient laboratory condition.

Part D: Scintillation efficiency

3.13 Scintillation efficiency

In evaluating the scintillating efficiency of each the 4-chloro-2,5-diphenyloxazole derivatives, the following scintillation counting experiments were undertaken. The ionizing radiation source chosen for this study was ^{36}Cl , a low energy β -particle emitter.

Preparation of compounds for assay. An oxazole derivatives were dissolved in 1% W/V of polyacrylate. 0.5 mL of these solutions were coated onto glass slide and then allowed to dry for one hour at room temperature.

Assay procedure. The ^{36}Cl radiation source and sample glass slide were equipped with photomultiplier tube. Each sample was counted for 4 minutes at 400 V. The averaged cpm results obtained, for each 4-chloro-2,5-diphenyloxazole derivatives at each concentration, are shown in **Figure 3.1**.



Figure 3.1: Scintillation instrument

Part E: Electrospinning

3.14 Electrospinning

Electrospinning was used as a novel and facile method to fabricate the optical polymer. The spin-dope solution, which consisted of a 20% by weight, solution of polymer, was dissolved in either polystyrene or polymethylmethacrylate. A live electrode wire from the DC power source was inserted into the pipette containing the spin dope. When the charge induced in the polymer solution overcame the surface tension of the liquid, a stream of polymer solution was produced. The fine fibers were collected on a glass slide. The applied electrospinning voltages ranged from 18-20 kV. The working distance between the tip of the pipette and the glass slide was 30 cm. The collection time was about 45-60 sec. The electrospun membranes were dried in a vacuum oven at 70°C for 24 h.



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