Supporting Information

Pyrene-Functionalized Ruthenium Nanoparticles: Novel Fluorescence Characteristics From Intraparticle Extended Conjugation

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Synthetic Procedures for Pyrene Derivatives

(i) 1-Vinylpyrene. The procedure of Cumming et al. was generally followed.[1] To a two-neck, round bottom flask under N_2 was added methyltriphenylphosphonium bromide (0.85 g, 2.4 mmol) and 18-crown-6 (18.0 mg, 0.07 mmol). A 1.0 M solution of potassium *t*-butoxide (2.4 mL, 2.4 mmol in THF) was added and the mixture was further diluted with THF (7.0 mL) and cooled to 0 ^{o}C. A solution of 1-pyrenecarboxaldehyde (0.50 g, 2.2 mmol) in THF (3.0 mL) was added drop-wise over 10 min to the cooled solution and was allowed to stir at room temperature overnight. The mixture was filtered and the filter cake dissolved in diethyl ether before being passed through a short bed of neutral alumina. Evaporation yielded a yellow solid, which was further purified to a white solid by flash column chromatography using hexanes as eluent (0.23 g, 47% yield); mp 86 – 88 ^{o}C (lit. 88 – 89 ^{o}C);[1] ^{1}H NMR (500 MHz, $CDCl_3$), 8.41 – 8.39 (d, J = 9.0 Hz, 1H), 8.22 – 8.20 (sext, J = 8.0, 4.5 Hz, 4H), 8.13 – 8.11 (d, J = 9.0 Hz, 1H), 8.05 (s, 2H), 8.02 – 7.99 (t, J = 7.5 Hz, 1H), 7.83 – 7.77 (dd, J = 11.0, 17.5 Hz, 1H), 6.02 – 5.98 (d, J = 17.0 Hz, 1H), 5.63 – 5.61 (d, J = 11.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$), 134.4, 132.6, 131.7, 131.2, 131.1, 128.3, 127.8, 127.6, 127.5, 126.2, 125.5, 125.2, 123.9, 123.3, 117.5.

(ii) 1-Allylpyrene. The procedure of Takuwa et al. was generally followed.[2] 1-Bromopyrene (100 mg, 0.35 mmol) was stirred in a mixture of anhydrous benzene and diethyl ether (4:1, 2.0 mL) in a two-neck, round bottom flask. The solution was stirred at room temperature under N_2 and *n*-BuLi (2.2 M in hexanes, 0.19 mL, 0.53 mmol) was added drop-wise, at which time the mixture became bright yellow. The solution was stirred for 30 min before adding freshly distilled allyl bromide. Following an additional 20 min of stirring, no solid remained in the yellow solution, which was then cooled to 0 ^{o}C and quenched with a saturated ammonium chloride solution. The reaction was extracted with ether (3 × 20 mL) and the combined organic layers were washed with water (30 mL), dried with $MgSO_4$, vacuum filtered, and evaporated to yield a yellow oil. Purification by flash column chromatography using hexanes as eluent yielded a pale-yellow oil, which was stored away from light, under nitrogen, and in a freezer (52.1 mg, 62% yield); ^{1}H NMR (500 MHz, $CDCl_3$), 8.29 – 8.27 (d, J = 9.5 Hz, 1H), 8.22 – 8.10 (m, 4H), 8.07 – 7.99 (m, 3H), 7.91 – 7.89 (d, J = 7.5 Hz, 1H), 6.27 – 6.20 (m, 1H), 5.16 – 5.13 (dq, J = 1.5, 10.0 Hz, 1H), 5.11 – 5.06 (dq, J = 2.0, 17.0 Hz, 1H), 4.14 – 4.12 (dt, J = 1.5, 6.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$), 137.5, 134.1, 131.6, 131.3, 131.1, 130.3, 129.1, 127.7, 127.60, 127.57, 127.5, 126.9, 126.0, 125.2, 125.1, 125.0, 124.9, 123.8, 116.3, 37.9.

(iii) 1-Hydroxymethylpyrene. The procedure of Malashikhin and Finney was generally followed.[3] To a round bottom flask charged with a stir bar, 1-pyrenecarboxaldehyde (0.50 g, 2.2 mmol) was stirred at 0 ^{o}C in THF. A solution of $NaBH_4$ (0.25 g, 6.5 mmol) in 95% ethanol (15

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mL) was prepared along with ten drops of 1 M NaOH. This solution was added to the aldehyde and stirred at 0 °C for 15 min and changed from a yellow-green color to milky-white. The mixture was quenched with 10% HCl (v/v), diluted with water (50 mL) and extracted with CH_2Cl_2 (3 × 30 mL). The combined organic fractions were washed with $NaHCO_3$ and water successively (30 mL each), and dried with $MgSO_4$. Filtration and evaporation afforded the desired alcohol, which was used without further purification (0.50 g, 98% yield); mp 122 – 123 °C (lit. 123 – 124 °C);[4] ^{1}H NMR (500 MHz, $CDCl_3$), 8.40 – 8.38 (d, J = 9.5 Hz, 1H), 8.22 – 8.16 (m, 4H), 8.08 – 8.16 (m, 4H), 5.43 – 5.42 (d, J = 5.5 Hz, 2H), 1.88 – 1.86 (t, J = 5.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$), 128.2, 127.8, 127.7, 126.3, 125.6, 125.0, 123.3, 64.1.

(iv) 1-Bromomethylpyrene. The procedure of Malashikhin and Finney was generally followed.[3] To a 2-neck round bottom flask under N_2 was added 1-hydroxymethylpyrene (0.50 g, 2.2 mmol) and pyridine (0.09 mL, 1.1 mmol) in anhydrous CH_2Cl_2 (40 mL). The clear solution was stirred at 0 °C and phosphorous tribromide (0.10 mL, 1.1 mmol) in CH_2Cl_2 (2.5 mL) was added drop-wise, at which point the solution became cloudy. After stirring for 3 h at 0 °C, the reaction was poured into a mixture of ice and CH_2Cl_2 (100 mL). The organic layer was washed with water, saturated $NaHCO_3$, and water (50 mL each). The organic layer was dried with $MgSO_4$, filtered and evaporated to give a pale-yellow solid, which was recrystallized from benzene. According to Geerts and Martin,[5] 1-bromomethylpyrene should be used immediately, as it is not stable (0.54 g, 85% yield), mp 134 – 135 °C (lit. 136 – 137 °C);[6] ^{1}H NMR (500 MHz, $CDCl_3$), 8.40 – 8.38 (d, J = 9.5 Hz, 1H), 8.26 – 8.22 (m, 3H), 8.13 – 8.02 (m, 5H), 5.27 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$), 132.1, 131.4, 130.9, 130.7, 129.2, 128.5, 128.40, 128.32, 128.26, 128.2, 128.0, 127.9, 127.7, 127.6, 127.5, 126.4, 125.8, 125.3, 125.0, 124.9, 124.8, 123.0, 32.4.

(v) Triphenyl(pyren-1-ylmethyl)phosphonium bromide. The procedure of Geerts and Martin was generally followed.[5] To a 2-neck round bottom flask under N_2 was added 1-bromomethylpyrene (0.50 g, 1.7 mmol) and recrystallized triphenylphosphine (0.45 g, 1.7 mmol) in toluene (16 mL). The reaction was stirred at reflux for 2 h in the dark. The product precipitated out of solution as a white solid and was vacuum filtered, washed with toluene, water and dried under vacuum (0.80 g, 85% yield); ^{1}H NMR (500 MHz, CD_3OD), 8.18 – 8.17 (d, J = 7.5 Hz, 1H), 8.07 – 8.04 (t, J = 8.0 Hz, 2H), 7.98 – 7.92 (m, 3H), 7.76 – 7.73 (m, 3H), 7.71 – 7.69 (dd, J = 2.5, 8.0 Hz, 1H), 7.66 (s, 2H), 7.59 – 7.50 (m, 12H), 5.58 – 5.55 (d, J = 14.5 Hz, 2H); ^{13}C NMR (125 MHz, CD_3OD), 136.5, 135.8, 135.6, 135.5, 133.1, 132.6, 132.1, 132.0, 131.6, 131.4, 131.3, 130.5, 130.4, 129.5, 129.2, 128.3, 127.8, 127.1, 126.8, 125.9, 125.2, 123.4, 121.7, 121.6, 119.3, 118.7, 28.7, 28.3.

(vi) (*E*)-1,2-di(pyren-1-yl)ethane. The procedure of Geerts and Martin[5] was generally followed. To a 2-neck round bottom flask under N_2 was added 1-pyrenecarboxaldehyde (0.22 mg, 0.94 mmol), triphenyl(pyren-1-ylmethyl)phosphonium bromide (0.72 g, 1.3 mmol), and absolute ethanol (25 mL). The mixture was stirred to dissolution prior to the addition of *t*-BuOK in THF (0.30 mL, 1.3 mmol, 20 wt%) at room temperature. Immediately upon the addition of the *t*-BuOK solution, the reaction became orange in color and was allowed to stir for 3 h in the dark. Filtration of the light orange solid and subsequent suspension in boiling water gave a yellow-orange solid, which was dried under vacuum. Trituration in hexanes and filtration gave a yellow powder. Extra care was taken to protect the product from exposure to light and excess heat (0.367 g, 91% yield); mp 306 – 308 °C (yellow to orange to brown; lit. 306.5 – 308 °C);[5] ^{1}H NMR (600 MHz, $CDCl_3$), 8.63 – 8.62 (d, J = 9.0 Hz, 1H), 8.56 – 8.55 (d, J = 7.8 Hz, 1H), 8.51 – 8.49 (d, J = 9.0 Hz, 1H), 8.46 (s, 1H), 8.29 – 8.27 (d, J = 8.4 Hz, 1H), 8.23 – 8.17 (m, 5H), 8.14 – 8.10 (m, 3H), 8.05 – 8.00 (m, 3H), 7.92 – 7.90 (d, J = 9.0 Hz, 1H), 7.82 (s, 1H), 7.73 – 7.71 (d,

J = 8.4 Hz, 1H), 7.61 – 7.60 (d, *J* = 8.4 Hz, 1H).

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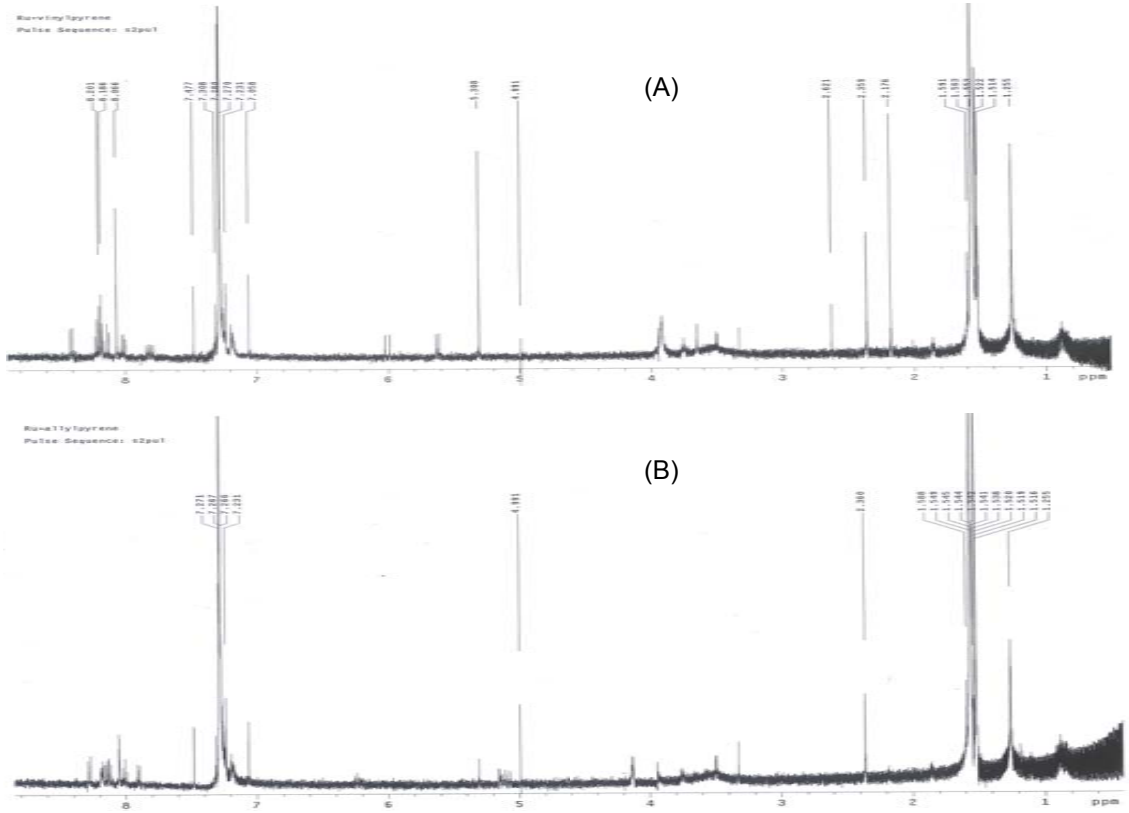

Figure S1. NMR spectra of the organic components of Ru=VPy and Ru=APy nanoparticles after the particle cores were dissolved by dilute KCN.

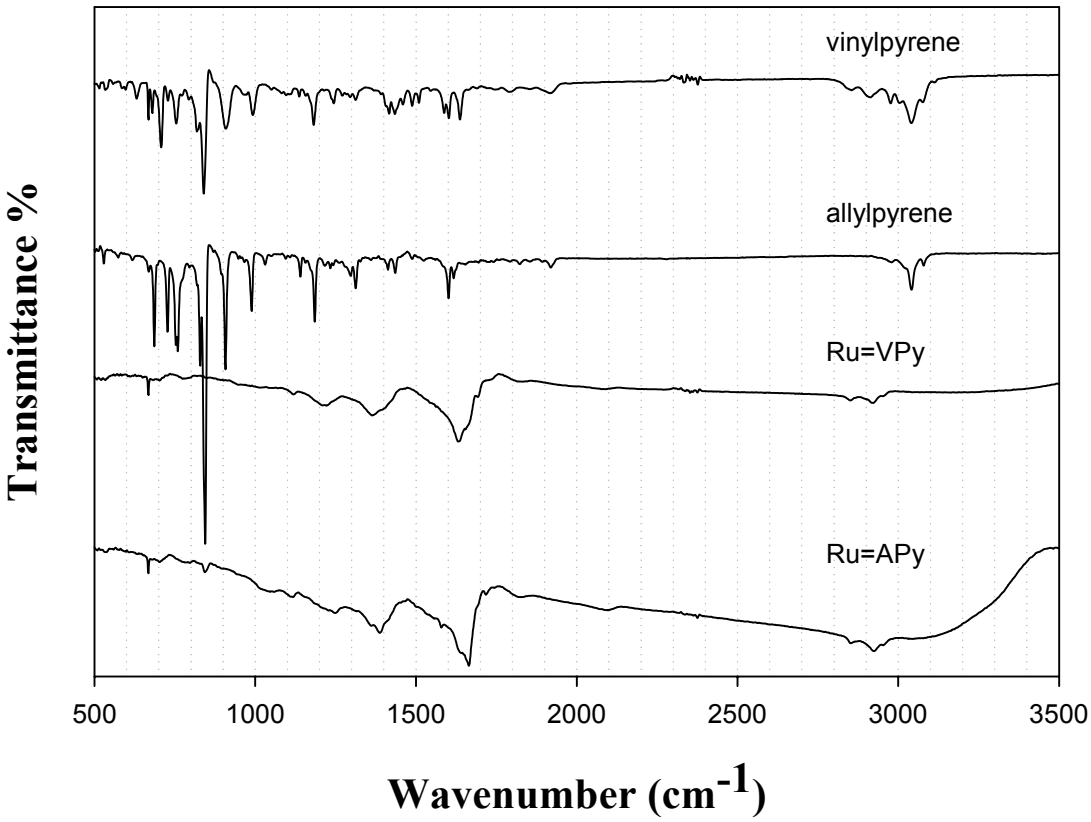

Figure S2. FTIR spectra of vinylpyrene, allylpyrene, Ru=VPy, and Ru=APy nanoparticles.