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Ru(II)–Polypyridine Complexes Covalently Linked to Electron Acceptors as Wires for Light–Driven Pseudorotaxane–Type Molecular Machines

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SUPPORTING INFORMATION

Experimental procedure

and characterization of the compounds.

Stability constants of pseudorotaxanes.

2–(2–Phenoxyethoxy)ethanol (10). Phenol (15.0 g, 0.16 mol) was added to a stirred solution of K_2CO_3 (63 g, 0.46 mol) in MeCN (200 mL) under nitrogen. The resulting mixture was heated under reflux for 3 h before being allowed to cool. A solution of 2–(2–chloroethoxy)ethanol (19.9 g. 0.16 mol) in MeCN (100 mL) was added dropwise with stirring and the resulting mixture heated under reflux for 5 days. The mixture was then filtered and the precipitate washed with CH_2Cl_2 (2 x 50 mL). The filtrate and washings were subsequently concentrated to 30 mL and diluted again with CH_2Cl_2 (50 mL). The organic phase was washed with HCl (3 M, 2 x 50 mL) and H_2O (50 mL), before being dried ($MgSO_4$). The mixture was filtered and the solvent removed to yield **10** (24.5 g, 84%) as a clear oil: EIMS: *m/z* 182 $[M+1]^+$; $C_{10}H_{14}O_3$ requires *m/z* 182.0943, found 182.0947; ^1H NMR (300 MHz, $CDCl_3$, 25°C): δ = 3.64 (2H, t, *J* = 4.5 Hz), 3.76 (2H, t, *J* = 4.5 Hz), 3.81 (2H, t, *J* = 4.5 Hz), 4.09 (2H, t, *J* = 4.5 Hz), 4.57 (1H, bs), 6.84–7.00 (3H, m), 7.15–7.32 (2H, m); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25°C): δ = 61.7, 67.4, 69.7, 72.6, 114.7, 121.1, 129.2, 158.7; $C_{10}H_{14}O_3$ (182.2): calcd C 65.92, H 7.74; found C 65.37, H 7.90.

(2–(2–Phenoxyethoxy)ethoxy) ^{1}–Toluenesulfonate (11). The alcohol **10** (22.5 g, 0.12 mol), NEt_3 (49.4 mL, 0.36 mmol), and DMAP (10 mg) were dissolved in dry CH_2Cl_2 (300 mL) and placed in an ice–bath. A solution of *p*–toluenesulfonyl chloride (30.5 g, 0.16 mmol) in CH_2Cl_2 (200 mL) was added dropwise with stirring during 3 h. The reaction vessel was placed in the refrigerator overnight, before being allowed to warm up to room temperature. The mixture was then filtered and the organic layer washed with HCl (3 M, 50 mL) and H_2O (50 mL), before being dried ($MgSO_4$). Removal of the solvent gave a colorless oil, which was subjected to chromatography (SiO_2, $CHCl_3$). Evaporation of the appropriate fractions gave a colorless oil which was characterized as **11** (36.5 g. 90%): CIMS: *m/z* 354 and 337 $([M+NH_4]^+$, [*M*+1]$^+$, respectively); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ = 2.37 (3H, m), 3.64–3.78 (4H, m). 4.00 (2H, t, *J* = 4.5 Hz), 4.17 (2H, t, *J* = 4.5 Hz), 6.84–6.96 (3H, m), 7.21–7.30 (4H, m), 7.77 (2H, d, *J* = 8.0 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25°C): δ = 67.3, 68.9, 69.4, 69.9, 114.6, 121.0, 127.9, 129.5, 129.9, 133.0, 144.9, 158.7; $C_{17}H_{20}O_5S$ (336.4): calcd C 60.70, H 5.99; found C 60.93, H 5.97.

4–(2–(2–(Ethoxy(ethoxyphenoxy))))benzyl Alcohol (12). 4–Hydroxybenzyl alcohol (18.6 g, 0.15 mol) and K_2CO_3 (63 g, 0.46 mol) were stirred in MeCN (400 mL) for 2 h under nitrogen. After heating the mixture up to reflux, the tosylate **11** (35.2 g, 0.10 mol) in MeCN (100 mL) was added and heating under reflux was continued for 4 days. The mixture was filtered upon cooling, and, after washing the residue with CH_2Cl_2 (100 mL), the solvent was removed to give an oily residue, which was subjected to chromatography (SiO_2, CH_2Cl_2 then CH_2Cl_2:Me_2CO 3:1), before being recrystallized (hexane/CH_2Cl_2) to give **12** (19.8 g, 70%) as a white crystalline solid: M.p. 108–110°C; EIMS: *m/z* 288 [*M*]$^+$; ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ = 2.17 (2H, s), 3.94 (4H. t, *J* = 4.5 Hz), 4.15 (4H, t, *J* = 4.5 Hz), 4.61 (1H, bs), 6.87–6.98 (5H, m), 7.26–7.32 (4H, m); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25°C): δ = 65.0, 67.4. 67.6. 69.9, 70.0. 114.7, 114.8. 120.9. 128.6. 129.4, 133.4, 158.4, 158.8. $C_{10}H_{20}O_4$ (204.3): calcd C 70.81, H 6.99; found C 70.57, H 6.88.

14·PF$_6$. A solution of **12** (1.00 g, 3.47 mmol) and C_5H_5N (0.30 g, 3.80 mmol) in CH_2Cl_2 (30 mL) was heated under reflux for 30 min under nitrogen. A solution of $SOCl_2$ (0.50 g, 4.16 mmol) in CH_2Cl_2 (20 mL) was added. After 4h of heating under reflux, the organic phase was washed with dilute HCl (2 M, 25 mL), before being dried ($MgSO_4$). Removal of the solvent gave an oil, which was subjected to chromatography (SiO_2, $CHCl_3$:MeOH 99:1). Evaporation of the appropriate fractions gave the benzyl chloride **13** (1.06 g, 100 %) (^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ = 3.92–3.98 (4H, m), 4.14–4.19 (4H, m), 4.59 (2H, s), 6.92–7.02 (5H, m), 7.29–7.37 (4H, m); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25°C): δ = 30.9, 65.0, 67.4, 67.6, 70.0, 114.7, 112.0, 128.6, 129.5, 129.8, 133.5, 158.4, 158.8) as a clear oil which was immediately used in the next step. The benzylic chloride **13** (1.06 g, 3.47 mmol) was mixed with 4,4'–bipyridine (1.53 g, 9.78 mmol) in MeCN (50 mL) and heated under reflux for 48 h. After filtration and removal of the solvent, the crude oily product was dissolved in H_2O (25 mL) with sufficient Me_2CO to achieve a solution, before being stirred with an excess of NH_4PF_6 overnight. On removal of the Me_2CO, the product oiled out. Excess of 4,4'–bipyridine was recovered (1.03 g, 55%) by dissolution in hot H_2O (3 x 100 mL) and separation from the product by filtration. The pure monoquat **14**·PF_6 (1.03 g, 55%) was isolated as a viscous solid oil, which solidified on standing. M.p. 65–67°C; FABMS: *m/z* 427, 271, and 157 ($[M–PF_6]^+$, $[M–bpy–PF_6]^+$, $[bpy]^+$, respectively); ^{1}H NMR (300 MHz, CD_3CN, 25°C): δ = 3.81–3.9 (4H. m), 4.04–4.09 (2H, m), 4.11–4.16 (2H, m), 5.67 (2H, s), 6.79–6.89 (3H, m), 6.95 and 7.43 (4H, AB, J_{AB} = 8.7 Hz), 7.12–7.23 (2H, m), 7.82–7.83 (2H, m), 8.24 and 8.81 (6H, AB, J_{AB} = 6.9 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25°C): δ = 64.9, 65.2, 68.5, 68.87, 70.4, 70.8, 115.6, 116.5, 116.6, 121.9, 123.0, 125.9, 127.2, 129.6, 130.6, 132.2, 142.3, 145.3, 145.7, 147.2, 151.7, 152.2, 159.9, 161.2, 161.3.

5–Bromomethyl–2,2'–bipyridine (15). A mixture of 5–methyl–2,2'–bipyridine (3.00 g, 0.02 mol), NBS (2.51 g, 0.01 mol) and AIBN (0.05 g, 0.30 mmol) in CH_2Cl_2 (100 mL) were warmed to 45°C for 48h. The solvent was removed *in vacuo* and the residue recrystallized from cyclohexane to yield **15** (1.63 g, 37%) as colorless crystals: M.p. 82–84°; FABMS: *m/z* 250 and 169 ($[M]^+$and $[M–Br]^+$ respectively); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ = 4.54 (2H, s), 7.30–7.36 (1H, m), 7.79–7.89 (2H, m), 8.38–8.41 (2H, m), 8.67–8.70 (2H, m);

^{13}C NMR (75.5 MHz, $CDCl_3$, 25°C): δ = 29.6, 121.0, 121.3, 123.9, 133.6, 137.0, 137.6, 149.3, 149.3, 155.5, 156.1.

16·2PF$_6$. The monoquat **14**·PF_6 (0.50 g, 0.87 mmol) and the bromide **15** (0.33 g, 1.40 mmol) were heated under reflux in MeCN (30 mL) overnight. The resultant precipitate was filtered and collected, before being stirred overnight with H_2O (50 mL), NH_4PF_6 (0.5 g) and sufficient Me_2CO to achieve dissolution. The Me_2CO was removed and the crude product **17**·2PF_6 separated by filtration. Purification by column chromatography (SiO_2: DMF–NH_4Cl (2 M, aq)–$MeNO_2$ 1:2:1), followed by (DMF–NH_4Cl (2 M, aq)–$MeNO_2$ 7:2:1), gave the desired diquat **16**·2PF_6 (0.14 g, 19%) as a bright yellow solid. M.p. 182–184°C decomp.; FABMS: *m/z* 887, 741, and 596 ([*M*]$^+$, [*M*–PF_6]$^+$, and [*M*–2PF_6]$^+$, respectively); ^{1}H NMR (300 MHz, CD_3CN, 25°C): δ = 3.82–3.88 (4H, m), 4.08–4.13 (2H, m), 4.15–4.18 (2H, m), 5.74 (2H, s), 5.91 (2H, s), 6.88–6.92 (3H, m), 7.00–7.04 (2H, m), 7.24–7.30 (2H, m), 7.40–7.46 (3H, m), 7.89 and 7.91 and 7.94 (1H, td, *J* = 7.8 Hz, *J* = 1.7 Hz), 7.97 and 8.00 (1H, dd, *J* = 8.3 Hz, *J* = 2.3 Hz). 8.33 and 8.37 (4H, dd, *J* = 12.2 Hz, *J* = 6.9 Hz), 8.42 (1H, δ, *J* = 8.0 Hz), 8.50 (1H. δ, *J* = 8.3 Hz), 8.66–8.88 (1H, m), 8.79 (1H, δ, *J* = 2.0 Hz,), 8.91 (4H, δ, *J* = 7.0 Hz), 9.00 (1H, δ, *J* = 7.0 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25°C): δ = 62.9, 65.2, 68.2, 68.6, 70.1, 70.3. 115.3, 116.3, 121.7, 122.0, 125.2, 128.2, 128.4, 128.4, 130.4, 132.2, 138.2. 139.1, 146.1, 146.6, 150.4, 150.9, 151.3, 151.4, 155.6, 158.1, 159.6, 161.0.

[(bpy)$_2$Ru(bpy)–CH$_2$–V–CH$_2$–R][PF$_6$]$_4$ (1·4PF$_6$). [Ru(bpy)$_2$Cl$_2$] (32 mg, 0.07 mmol) and $AgPF_6$ (64 mg, 0.10 mmol) were heated under reflux in Me_2CO (8 mL) for 2h. Following filtration of the precipitated AgCl, the "solvo–complex" was added dropwise to a refluxing solution of **17**·2PF_6 (0.05 g, 0.06 mmol) in Me_2CO (8 mL), and heating was continued for 1 h. On removal of the Me_2CO and addition of H_2O (5 mL), the orange–red precipitate was filtered, washed with H_2O (5 mL) and Et_2O (5 mL), and dissolved in MeCN (25 mL). After filtration, the solvent was removed and the product was subjected to column chromatography (SiO_2, DMF : NH_4Cl (2 M, aq) : $MeNO_2$ 7:2:1) to give **1**·$4PF_6$ (61 mg, 68%) as an orange–red solid. M.p. 161–163°C; FABMS: *m/z* : 1445 and 1300 ($[M–PF_6]^+$ and $[M–2PF_6]^+$); ^1H NMR (300 MHz, CD_3CN, 25°C): δ = 3.82–3.88 (4H, m), 4.09–4.13 (2H, m), 4.14–4.18 (2H, m), 5.69 (2H, s), 5.76 (2H, s), 6.89–6.97 (3H, m), 7.05 and 7.47 (3H, AB, J_{AB} = 9.0 Hz), 7.25–7.31 (1H, m), 7.35–7.44 (7H, m), 7.63–7.70 (2H, m), 7.71–7.75 (2H, m), 7.79–7.82 (2H, m), 7.92 and 7.95 (1H, dd, *J* = 8.0 Hz, *J* = 2.0 Hz), 7.99–8.11 (5H, m), 8.33–8.39 (4H, m), 8.46–8.55 (6H, m), 8.61 (2H, δ, *J* = 7.0 Hz), 8.95 (2H, δ, *J* = 7.0 Hz); ^{13}C NMR (75.5 MHz, CD_3Cl, 25°C): δ = 61.7, 68.3, 68.8, 70.3, 70.5, 115.5, 116.5, 121.8, 125.4, 126.0, 128.3, 128.5, 128.6, 129.1, 130.5, 132.3, 133.3, 138.7, 138.9, 146.4. 147.1, 152.5, 152.7, 152.9, 153.0.

5–(4–Bromobutyl)–2,2'–bipyridine (18). A solution of 5–methyl–2,2'–bipyridine (2.31 g, 13.6 mmol) in dry THF (50 ml) was added dropwise (30 min) at –78°C and under nitrogen to a stirred solution of freshly prepared LDA [from *i*–Pr_2NH (2 ml, 14.3 mmol) and *n*–BuLi (1.6 M in hexane, 8.75 ml, 14.0 mmol) in dry THF at –78°C] resulting in a dark brown–red solution. The mixture was allowed to warm up to 0°C before being stirred further at this temperature for 1.5 h. A solution of 1,3–dibromopropane (9.1 g, 45.0 mmol) in dry THF (40 ml) was added at once, making the reaction mixture dark blue. After 2 days of stirring at room temperature, the brownish–orange solution was quenched with MeOH (3 ml) and concentrated *in vacuo*. The residue was dissolved in EtOAc and washed with H_2O and brine, before being dried ($MgSO_4$). The solvent was evaporated off and the residue was purified by flash column chromatography (SiO_2, CH_2Cl_2 : MeOH : NH_4OH 100:1:0.1) to afford **18** (2.5 g, 63%) as a slightly yellow thick oil that solidified on standing.

EIMS (70 eV): *m/z* (%): 290 (28) [*M*]$^+$, 210 (5), 170 (100), 155 (15), 142 (37), 128 (15); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ = 1.74–1.97 (4H, m), 2.69 (2H, t, *J* = 7.4 Hz), 3.42 (2H, t, *J* = 6.4 Hz), 7.25–7.30 (1H, m), 7.62 (1H, dd, *J* = 8.1 Hz, *J* = 2.2 Hz); 7.79 (1H, dt, *J* = 7.7 Hz, *J* = 1.5 Hz), 8.30 (1H, d, *J* = 8.5 Hz), 8.34 (1H, d, *J* = 7.7 Hz), 8.49 (1H, d, *J* = 1.8 Hz), 8.65 (1H, d, *J* = 4.1 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25°C): δ = 29.4, 31.9, 32.0, 33.4, 120.8, 120.8, 123.5, 136.8, 136.9, 149.2, 149.3, 137.2, 154.2, 156.1; $C_{14}H_{15}BrN_2$ (291.2) calcd C 57.75, H 5.19, N 9.62; found C 57.89, H 5.36, N 9.59. A later fraction (eluent CH_2Cl_2–MeOH–NH_4OH (2 M) 100:2.5:0.5) gave 1,5–bis(2,2'–bipyrid–5–yl)pentane (0.4 g, 15%), m.p. 117°C, as white needles. EIMS (70 eV): *m/z* (%): 380 (99) [*M*]$^+$, 337 (9), 211 (79), 197 (20), 183 (55), 170 (100), 140 (20).; ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ = 1.42 (2H, quintet), 1.69 (4H, quintet), 2.65 (t, *J* = 7.7 Hz, 4H), 7.25–7.29 (2H, m), 7.61 (2H, dd, *J* = 8.1 Hz, *J* = 2.2 Hz), 7.79 (2H, dt, *J* = 7.7 Hz, *J* = 1.8 Hz), 8.29 (2H, d, *J* = 8.1 Hz), 8.34 (2H, d, *J* = 7.7 Hz), 8.49 (2H, s), 8.65 (2H, d, *J* = 4.4 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25°C): δ = 28.6, 30.9, 32.7, 120.7, 120.8, 123.4, 136.8, 136.9, 149.1, 149.3, 137.9, 153.9, 156.2; $C_{25}H_{24}N_4$ (380.5) calcd C 78.92, H 6.36, N 14.72; found C 79.02, H 6.47, N 14.89.

19·2PF$_6$. A mixture of **18** (290 mg, 1.0 mmol) and 1–ethyl–4,4'–bipyridinium [PF_6^-] **17**·PF_6 (330 mg, 1.0 mmol) in 10 ml of MeCN was refluxed for 4 days under nitrogen. The solvent was then removed in vacuo and the residue was subjected to column chromatography (SiO_2, MeOH : NH_4Cl (2 M) : $MeNO_2$ 7:2:1). The fractions containing the product were concentrated *in vacuo*, before being treated with 50% aqueous solution NH_4PF_6. The resulting white precipitate was filtered off, washed with H_2O, Et_2O, and dried *in vacuo* (70°C / 0.1 torr) to give the quarternary salt **19**·2PF_6 (0.47 g, 69%), M.p. 248–249°C. LSIMS: *m/z*: 687 [*M*+H]$^+$, 541 [*M*–PF_6]$^+$, 396 [*M*–2PF_6]$^+$; ^{1}H NMR (300 MHz, CD_3CN, 25°C): δ = 1.65 (3H, t, *J* = 7.4 Hz), 1.77 (2H, quintet), 2.09 (2H, quintet), 2.83 (2H, t, *J* = 7.7 Hz), 4.59–4.76 (4H, m), 7.57 (1H, t, *J* = 6.1 Hz), 7.93 (1H, d, *J* = 8.1 Hz), 8.09 (1 H, t, *J* = 7.7 Hz), 8.30–8.46 (6H, m), 8.58 (1H, s), 8.70 (1H, d, *J* = 4.4 Hz), 8.88 (2H, d, *J* = 6.6 Hz), 8.91 (2H, d, *J* = 7.0); ^{13}C NMR (75.5 MHz, CD_3CN, 25°C): δ = 16.5, 27.7, 31.3, 32.3, 58.6, 62.7, 122.3, 122.4, 126.1, 128.0, 128.1, 140.3, 140.7, 146.2, 146.4, 148.9, 150.9, 153.0 (Cq).

[(Me$_2$bpy)$_2$Ru(bpy)–(CH$_2$)$_4$–V–CH$_2$–Me][PF$_6$]$_4$ (2·4PF$_6$). A mixture of the Ru(Me$_2$bpy)Cl$_2$ (93 mg, 0.172 mmol) and **19**·2PF$_6$ (118 mg, 0.172 mmol) in EtOH / H_2O (3:1, *v/v*, 24 ml) was heated under reflux and over an atmosphere of nitrogen for 20 h. The solvent was evaporated under vacuum and the residue was purified by flash column chromatography (SiO_2, MeOH : NH_4Cl (2 M) : $MeNO_2$ 7:2:1). The fractions containing the Ru(II) complex were combined, and concentrated *in vacuo*. The solid was dissolved in H_2O and treated with an excess of 50% NH_4PF_6 solution. The precipitate was filtered off, washed with H_2O and dried (70°C / 0.1 torr) to afford **2**·4PF$_6$ (176 mg, 71%), as an orange solid, M.p. 152–154°C (dec.). LSIMS: *m/z*: 1301 [*M*–PF$_6$]$^+$, 1156 [*M*–2PF$_6$]$^+$, 1011 [*M*–3PF$_6$]$^+$; ^{1}H NMR (300 MHz, CD_3CN, 25°C): δ = 1.57 (m, 2H), 1.66 (3H, t, *J* = 7.4 Hz), 2.17 (2H, m), 2.46–2.60 (2H, m), 2.52 (12H, s), 4.56 (2H, t, *J* = 7.5 Hz), 4.68 (2H, q, *J* = 7.4 Hz), 7.17–7.28 (4H, m), 7.39 (1H, t, *J* = 6.2 Hz), 7.45–7.59 (5H, m), 7.69 (1H, d, *J* = 5.5 Hz), 7.89 (1H, d, *J* = 7.0 Hz), 8.01 (1H, t, *J* = 7.7 Hz), 8.30–8.49 (m, 10H), 8.86 (2H, d, *J* = 6.6 Hz), 8.93 (2H, d, *J* = 6.6 Hz); ^{13}C NMR (75.5 MHz, CD_3CN, 25°C): δ = 16.4, 21.1, 27.0, 31.2, 32.0, 58.6, 62.5, 124.6, 125.7, 128.0, 129.1, 138.0, 138.2, 146.3, 151.3, 151.4, 151.5, 151.6, 151.8, 152.2, 142.8, 150.7, 150.9, 151.0, 155.9, 157.4, 157.5, 158.1; $C_{50}H_{52}F_{24}N_8P_4Ru$ (1445.95): calcd C 41.53, H 3.62, N 7.75; found C 41.49, H 3.63, N 7.62.

20·2PF$_6$. To a solution of [Ru(tpy)Cl$_3$] (0.110 g, 0.248 mmol) and 4'–(*p*–bromomethylphenyl)–2,2':6',2''–terpyridine (0.100 g, 0.248 mmol) in EtOH (20 mL) was added a few drops of N–ethylmorpholine added. The solution was heated under reflux for 1.5 h, filtered through celite and the filtrate treated with methanolic ammonium hexafluorophosphate and H_2O (60 mL). The resultant fine solid was collected over celite, washed with H_2O and a little EtOH and dried *in vacuo*. The celite was extracted with MeCN and the solvent evaporated *in vacuo* to give **20**·2PF$_6$ as a red solid (0.234 g, 92%); FABMS: *m/z* 883, 738 ([*M*–PF$_6$]$^+$, and [*M*–2PF$_6$]$^+$); ^{1}H NMR (300 MHz, CD$_3$CN, 25°C): δ = 4.84 (2H, s), 7.15–7.21 (4H, m), 7.36–7.38 (2H, m), 7.43–7.46 (2H, m), 7.79 (2H, d, J_{AB} = 8.5 Hz), 7.88–7.97 (4H, m), 8.19–8.24 (2H, m), 8.42 (1H, t, J_{AB} = 8.2 Hz), 8.51 (2H, d, J_{AB} = 8.0 Hz), 8.63–8.67 (2H, m), 8.74–8.78 (2H, m), 9.0 (2H, s); ^{13}C NMR (75.5 MHz, CD$_3$CN, 25°C): δ = 46.6, 122.5, 124.7, 125.5, 128.6, 129.5, 130.9, 136.8, 139.0, 141.2, 153.4, 156.3, 156.4, 159.0, 159.1.

21·3PF$_6$. A solution of [Ru(tpy)–C$_6$H$_4$–CH$_2$Br] **20**·2PF$_6$ (0.103 g, 0.10 mmol), diazapyrene (0.031 g, 0.15 mmol) and lithium bromide (0.087 g, 1.00 mmol) in MeCN (10 mL) were heated under reflux for 3 days. The solvent was removed *in vacuo* and the residue was purified by flash column chromatography (SiO_2, MeOH:NH_4Cl (2 M, aq):$MeNO_2$ 7:2:1). The fractions containing the product were concentrated *in vacuo* before being treated with an excess of 50% NH_4PF_6 aqueous solution. The resulting red precipitate was filtered, washed with H_2O and Et_2O and dried *in vacuo* to give the salt **21**·3PF$_6$ (0.026 g; 20%); FABMS: *m/z* 1151.1 ([*M*–PF$_6$]$^+$); ^{1}H NMR (300 MHz, CD$_3$CN, 25°C): δ = 6.39 (2H, s), 7.13–7.19 (5H, m), 7.35 (2H, d, J_{AB} = 5.3 Hz), 7.40 (2H, d, J_{AB} = 5.5 Hz), 7.88–7.97 (7H, m), 8.32 (2H, d, J_{AB} = 8.4 Hz), 8.41 (1H, t, J_{AB} = 8.0 Hz); 8.49 (2H, d, J_{AB} = 8.0 Hz); 8.62–8.65 (4H, m), 8.74–8.81 (4H, m), 8.99 (2H, s), 9.89 (2H, s); ^{13}C NMR (75.5 MHz, CD$_3$CN, 25°C): δ = 54.9, 122.4, 124.5, 125.2, 125.3, 127.7, 128.2, 128.3, 129.5, 130.4, 131.3, 132.0, 136.3, 136.7, 138.8, 138.9, 139.0, 140.0, 146.7, 147.7, 153.1, 153.3, 156.1, 156.4, 158.8.

[(tpy)Ru(tpy)–C_6H_4–CH_2–DAP–CH_2–R][PF_6]$_4$ (3·4PF_6). A solution of **21**·3PF_6 (0.041 g, 0.03 mmol), **13** (0.432 g, 1.41 mmol) and lithium bromide (0.245 g, 2.82 mmol) in CH_3CN (20 mL) was heated under reflux under an atmosphere of N_2 for 3 days. The solvent was evaporated *in vacuo* and the residue purified by flash column chromatography (SiO_2, MeOH:NH_4Cl (2 M, aq):$MeNO_2$ 7:2:1). The fractions containing the product were concentrated *in vacuo* before being treated with an excess of 50% NH_4PF_6 aqueous solution. The resulting red precipitate was filtered, washed with H_2O and Et_2O and dried *in vacuo* to afford the salt **3**·4PF_6 (0.025 g; 49%); FABMS: *m/z* 1567.6 ([*M*–PF_6]$^+$); 1422.4 ([*M*–2PF_6]$^+$); 1278.3 ([*M*–3PF_6]$^+$); ^{1}H NMR (300 MHz, CD_3CN, 25°C) δ = 3.81–3.85 (4H, m), 4.09 (2H, t, J_{AB} = 4.6 Hz), 4.17 (2H, t, J_{AB} = 4.6 Hz), 6.20 (2H, s), 6.44 (2H, s), 6.87–6.90 (2H, m), 7.07 (2H, d, J_{AB} = 8.7 Hz), 7.12–7.17 (5H, m), 7.23–7.26 (2H, m), 7.33 (2H, d, J_{AB} = 5.5 Hz),), 7.37 (2H, d, J_{AB} = 5.5 Hz), 7.60 (2H, d, J_{AB} = 8.7 Hz), 7.88–7.93 (4H, m), 7.96 (2H, d, J_{AB} = 8.3 Hz), 8.31 (2H, d, J_{AB} = 8.4 Hz), 8.40 (1H, t, J_{AB} = 8.1 Hz), 8.47 (2H, t, J_{AB} = 8.1 Hz), 8.61 (2H, t, J_{AB} = 7.9 Hz), 8.74 (2H, t, J_{AB} = 8.1 Hz), 8.83–8.89 (4H, m), 8.97 (2H, s), 9.93 (2H, s),10.10 (2H, s).

Stability constants (K_a) and derived free energies of complexation ($–\Delta G^o$) for the 1:1 complexes formed between BPP34C10 **8** or 1/5DN38C10 **9** and bipyridinium–based thread–type compounds in MeCN.

1:1 complex	K_a (M^{-1})	$\angle\Delta G^o$ (kcal mol^{-1})
[**16•8**][2PF_6]	228 ± 10 [a,e]	3.2 ± 0.1
[Me–V–Me•**8**][PF_6]$_2$	240 ± 36 [a]	3.3 ± 0.1
[Me–V–Me•**8**][PF_6]$_2$	226 ± 20 [b,e]	3.2 ± 0.1
[Me–V–Me•**9**][PF_6]$_2$	668 ± 27 [c,e]	3.8 ± 0.1
[$PhCH_2$–V–CH_2Ph•**8**][PF_6]$_2$	558 ± 24 [d,e]	3.7 ± 0.1

[a] Determinations based on observing changes in the chemical shifts ($\Delta\delta$) of solutions where the relative concentration of both components is maintained constant and equal to each other and measured at 300 K. [b] Determined spectophotometrically at λ = 437 nm. The data was subjected to Benesi–Hildebrand treatment. [c] Determined by spectophotometrical titration at λ = 482 nm. [d] Determined by spectophotometrical titration at λ = 505 nm. [e] The data (measured at 298 K) was treated on the non–linear curve fitting program Ultrafit (ref 28).