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$_2$CO$_3$ (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$_2$Cl$_2$ (2 x 50 mL). The filtrate and washings were subsequently concentrated to 30 mL and diluted again with CH$_2$Cl$_2$ (50 mL). The organic phase was washed with HCl (3 M, 2 x 50 mL) and H$_2$O (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$^+$]$^+$; C$_{10}$H$_{14}$O$_3$ requires m/z 182.0943, found 182.0947; $^1$H NMR (300 MHz, CDCl$_3$, 25°C): $\delta$ = 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): $\delta$ = 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$_2$Cl$_2$ (300 mL) and placed in an ice–bath. A solution of p–toluenesulfonyl chloride (30.5 g, 0.16 mmol) in CH$_2$Cl$_2$ (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$_2$O (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$_4$]$^+$,
4–(2–(2–(Ethoxy(ethoxyphenoxy))))benzyl Alcohol (12). 4–Hydroxybenzyl alcohol (18.6 g, 0.15 mol) and K₂CO₃ (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 CH₂Cl₂ (100 mL), the solvent was removed to give an oily residue, which was subjected to chromatography (SiO₂, CH₂Cl₂ then CH₂Cl₂:Me₂CO 3:1), before being recrystallized (hexane/CH₂Cl₂) to give 12 (19.8 g, 70%) as a white crystalline solid: M.p. 108–110°C; EIMS: m/z 288 [M]+; ¹H NMR (300 MHz, CDCl₃, 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); ¹³C NMR (75.5 MHz, CDCl₃, 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. C₁₀H₂₀O₄ (204.3): calcd C 70.81, H 6.99; found C 70.57, H 6.88.

14·PF₆. A solution of 12 (1.00 g, 3.47 mmol) and C₅H₅N (0.30 g, 3.80 mmol) in CH₂Cl₂ (30 mL) was heated under reflux for 30 min under nitrogen. A solution of SOCl₂ (0.50 g, 4.16 mmol) in CH₂Cl₂ (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 (MgSO₄). Removal of the solvent gave an oil, which was subjected to chromatography (SiO₂, CHCl₃: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): \(\delta = 3.92–3.98\) (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): \(\delta = 30.9, 65.0, 67.4, 67.6, 70.0, 114.7, 112.0, 128.6, 129.5, 129.8, 133.5, 158.4, 158.8\) 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\(_2\)O (25 mL) with sufficient Me\(_2\)CO to achieve a solution, before being stirred with an excess of NH\(_4\)PF\(_6\) overnight. On removal of the Me\(_2\)CO, the product oiled out. Excess of 4,4′–bipyridine was recovered (1.03 g, 55%) by dissolution in hot H\(_2\)O (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\(_3\)CN, 25°C): \(\delta = 3.81–3.9\) (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): \(\delta = 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\(_2\)Cl\(_2\) (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°C; FABMS: \(m/z\) 250 and 169 ([M]\(^{+}\)and [M–Br]\(^{+}\) respectively); \(^{1}H\) NMR (300 MHz, CDCl\(_{3}\), 25°C): \(\delta = 4.54\) (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$_2$O (50 mL), NH$_4$PF$_6$ (0.5 g) and sufficient Me$_2$CO to achieve dissolution. The Me$_2$CO was removed and the crude product 17·2PF$_6$ separated by filtration. Purification by column chromatography (SiO$_2$: DMF–NH$_4$Cl (2 M, aq)–MeNO$_2$ 1:2:1), followed by (DMF–NH$_4$Cl (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$_3$CN, 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.

$$[(\text{bpy})_2 \text{Ru(bpy)}–\text{CH}_2–\text{V–CH}_2–\text{R}]\text{[PF}_6\text{]}_4 \ (1\cdot4\text{PF}_6).$$  
[Ru(bpy)$_2$Cl$_2$] (32 mg, 0.07 mmol) and AgPF$_6$ (64 mg, 0.10 mmol) were heated under reflux in Me$_2$CO (8 mL) for 2h. Following filtration of the precipitated AgCl, the “solvocomplex” was added dropwise to a refluxing solution of 17·2PF$_6$ (0.05 g, 0.06 mmol) in Me$_2$CO (8 mL), and heating was continued for 1 h. On removal of the Me$_2$CO and addition of H$_2$O (5 mL), the orange–red precipitate was
filtered, washed with H₂O (5 mL) and Et₂O (5 mL), and dissolved in MeCN (25 mL). After filtration, the solvent was removed and the product was subjected to column chromatography (SiO₂, DMF : NH₄Cl (2 M, aq) : MeNO₂ 7:2:1) to give 1·4PF₆ (61 mg, 68%) as an orange–red solid. M.p. 161–163°C; FABMS: m/z: 1445 and 1300 ([M–PF₆]⁺ and [M–2PF₆]⁺); ¹H NMR (300 MHz, CD₃CN, 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); ¹³C NMR (75.5 MHz, CD₃Cl, 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–Pr₂NH (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 H₂O and brine, before being dried (MgSO₄). The solvent was evaporated off and the residue was purified by flash column chromatography (SiO₂, CH₂Cl₂ : MeOH : NH₄OH 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); 1H NMR (300 MHz, CDCl₃, 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); 13C NMR (75.5 MHz, CDCl₃, 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; C₁₄H₁₅BrN₂ (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 (elucent CH₂Cl₂–MeOH–NH₄OH (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); 1H NMR (300 MHz, CDCl₃, 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); 13C NMR (75.5 MHz, CDCl₃, 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; C₂₅H₂₄N₄ (380.5) calcd C 78.92, H 6.36, N 14.72; found C 79.02, H 6.47, N 14.89.

**19·2PF₆.** A mixture of 18 (290 mg, 1.0 mmol) and 1–ethyl–4,4’–bipyridinium [PF₆]⁻ 17·PF₆ (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 (SiO₂, MeOH : NH₄Cl (2 M) : MeNO₂ 7:2:1). The fractions containing the product were concentrated *in vacuo* before being treated with 50% aqueous solution NH₄PF₆. The resulting white precipitate was filtered off, washed with H₂O, Et₂O, and dried *in vacuo* (70°C / 0.1 torr) to give the quarternary salt 19·2PF₆ (0.47 g, 69%), M.p. 248–249°C. LSIMS: m/z: 687 [M+H]+, 541 [M–PF₆]+, 396 [M–2PF₆]+; 1H NMR (300 MHz, CD₃CN, 25°C): δ = 1.65 (3H, t, J = 7.4 Hz), 1.77 (2H, quintet), 2.09 (2H,
quintet), 2.83 (2H, \( J = 7.7 \) 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 (1H, \( t, J = 7.7 \) 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\(_3\)CN, 25°C): \( \delta = 16.5, 27.7, 31.3, 32.3, 58.6, 62.7, 122.3, 122.4, 126.1, 128.0, 128.1, 140.3, 140.7, 146.2, 146.4, 148.9, 150.9, 153.0 \) (Cq).

\[(\text{Me}_2\text{bpy})_2\text{Ru(bpy)}-\text{(CH}_2\text{)}_4-\text{V}-\text{CH}_2-\text{Me}\][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\(_2\)O (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\(_4\)Cl (2 M) : MeNO\(_2\) 7:2:1). The fractions containing the Ru(II) complex were combined, and concentrated \textit{in vacuo}. The solid was dissolved in H\(_2\)O and treated with an excess of 50% NH\(_4\)PF\(_6\) solution. The precipitate was filtered off, washed with H\(_2\)O 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\(_3\)CN, 25°C): \( \delta = 1.57 \) (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\(_3\)CN, 25°C): \( \delta = 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\(_8\)P\(_4\)Ru (1445.95): calcd C 41.53, H 3.62, N 7.75; found C 41.49, H 3.63, N 7.62.
20·2PF₆. To a solution of [Ru(tpy)Cl₃] (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 H₂O (60 mL). The resultant fine solid was collected over celite, washed with H₂O and a little EtOH and dried in vacuo. The celite was extracted with MeCN and the solvent evaporated in vacuo to give 20·2PF₆ as a red solid (0.234 g, 92%); FABMS: m/z 883, 738 ([M–PF₆]⁺, and [M–2PF₆]⁺); ¹H NMR (300 MHz, CD₃CN, 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, Jₐb = 8.5 Hz), 7.88–7.97 (4H, m), 8.19–8.24 (2H, m), 8.42 (1H, t, Jₐb = 8.2 Hz), 8.51 (2H, d, Jₐb = 8.0 Hz), 8.63–8.67 (2H, m), 8.74–8.78 (2H, m), 9.0 (2H, s); ¹³C NMR (75.5 MHz, CD₃CN, 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.

21·3PF₆. A solution of [Ru(tpy)--C₆H₄–CH₂Br]·20·2PF₆ (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 (SiO₂, MeOH:NH₄Cl (2 M, aq):MeNO₂ 7:2:1). The fractions containing the product were concentrated in vacuo before being treated with an excess of 50% NH₄PF₆ aqueous solution. The resulting red precipitate was filtered, washed with H₂O and Et₂O and dried in vacuo to give the salt 21·3PF₆ (0.026 g; 20%); FABMS: m/z 1151.1 ([M–PF₆]⁺); ¹H NMR (300 MHz, CD₃CN, 25°C): δ = 6.39 (2H, s), 7.13–7.19 (5H, m), 7.35 (2H, d, JₐB = 5.3 Hz), 7.40 (2H, d, JₐB = 5.5 Hz), 7.88–7.97 (7H, m), 8.32 (2H, d, JₐB = 8.4 Hz), 8.41 (1H, t, JₐB = 8.0 Hz); 8.49 (2H, d, JₐB = 8.0 Hz); 8.62–8.65 (4H, m), 8.74–8.81 (4H, m), 8.99 (2H, s), 9.89 (2H, s); ¹³C NMR (75.5 MHz, CD₃CN,
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.

\[([\text{tpy}]\text{Ru(tpy)}-\text{C}_6\text{H}_4-\text{CH}_2-\text{DAP-CH}_2-R)[\text{PF}_6]_4 \ (3\cdot4\text{PF}_6)\] A solution of 21⋅3PF₆ (0.041 g, 0.03 mmol), 13 (0.432 g, 1.41 mmol) and lithium bromide (0.245 g, 2.82 mmol) in CH₃CN (20 mL) was heated under reflux under an atmosphere of N₂ for 3 days. The solvent was evaporated in vacuo and the residue purified by flash column chromatography (SiO₂, MeOH:NH₄Cl (2 M, aq):MeNO₂ 7:2:1). The fractions containing the product were concentrated in vacuo before being treated with an excess of 50% NH₄PF₆ aqueous solution. The resulting red precipitate was filtered, washed with H₂O and Et₂O and dried in vacuo to afford the salt 3⋅4PF₆ (0.025 g; 49%); FABMS: m/z 1567.6 ([M–PF₆]+); 1422.4 ([M–2PF₆]+); 1278.3 ([M–3PF₆]+); \(^1\)H NMR (300 MHz, CD₃CN, 25°C) δ = 3.81–3.85 (4H, m), 4.09 (2H, t, Jₐₙₐ = 4.6 Hz), 4.17 (2H, t, Jₐₙₐ = 4.6 Hz), 6.20 (2H, s), 6.44 (2H, s), 6.87–6.90 (2H, m), 7.07 (2H, d, Jₐₙₐ = 8.7 Hz), 7.12–7.17 (5H, m), 7.23–7.26 (2H, m), 7.33 (2H, d, Jₐₙₐ = 5.5 Hz), 7.37 (2H, d, Jₐₙₐ = 5.5 Hz), 7.60 (2H, d, Jₐₙₐ = 8.7 Hz), 7.88–7.93 (4H, m), 7.96 (2H, d, Jₐₙₐ = 8.3 Hz), 8.31 (2H, d, Jₐₙₐ = 8.4 Hz), 8.40 (1H, t, Jₐₙₐ = 8.1 Hz), 8.47 (2H, t, Jₐₙₐ = 8.1 Hz), 8.61 (2H, t, Jₐₙₐ = 7.9 Hz), 8.74 (2H, t, Jₐₙₐ = 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 (−$\Delta G^0$) for the 1:1 complexes formed between BPP34C10 8 or 1/5DN38C10 9 and bipyridinium–based thread–type compounds in MeCN.

<table>
<thead>
<tr>
<th>1:1 complex</th>
<th>$K_a$ (M$^{-1}$)</th>
<th>$\angle\Delta G^0$ (kcal mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[16•8][2PF$_6$]</td>
<td>228 ± 10 [a,e]</td>
<td>3.2 ± 0.1</td>
</tr>
<tr>
<td>[Me–V–Me•8][PF$_6$]$_2$</td>
<td>240 ± 36 [a]</td>
<td>3.3 ± 0.1</td>
</tr>
<tr>
<td>[Me–V–Me•8][PF$_6$]$_2$</td>
<td>226 ± 20 [b,e]</td>
<td>3.2 ± 0.1</td>
</tr>
<tr>
<td>[Me–V–Me•9][PF$_6$]$_2$</td>
<td>668 ± 27 [c,e]</td>
<td>3.8 ± 0.1</td>
</tr>
<tr>
<td>[PhCH$_2$–V–CH$_2$Ph•8][PF$_6$]$_2$</td>
<td>558 ± 24 [d,e]</td>
<td>3.7 ± 0.1</td>
</tr>
</tbody>
</table>

[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 spectrophotometrically at $\lambda = 437$ nm. The data was subjected to Benesi–Hildebrand treatment.  
[c] Determined by spectrophotometrical titration at $\lambda = 482$ nm.  
[d] Determined by spectrophotometrical titration at $\lambda = 505$ nm.  
[e] The data (measured at 298 K) was treated on the non–linear curve fitting program Ultrafit (ref 28).