Supporting Information:

Table 1: ^{1}H-NMR chemical shifts (ppm) for the $[Ru(bpy)_2Cl(BPEB)]PF_6$ and $[\{Ru(bpy)_2Cl\}_2(BPEB)](PF_6)_2$ complexes in $(CD_3)_2CO$.

Proton	δ (ppm)			
	Mononuclear	Binuclear	Free Ligand[(a)]	$[Ru(bpy)_3]^{+2}$ [(b)]
	1,4-bis[2-(4-pyridyl)ethenyl]benzene			
H_α	-	-	7.39 (4H, d, *J= 5.8 Hz*)	-
H_β	7.49 (2H, d, *J=6.5 Hz)*	7.49 (4H, d, *J=6.4 Hz*)	7.39 (4H, d, *J= 6.0 Hz*)	-
Hγ	7.69 (2H, d, *J=8.6 Hz*)	7.66 (4H, s)	7.80 (4H, s)	-
$H_{\omega1}$	7.26 (2H, d, *J=16.4 Hz)*	7.27 (2H, d, *J=16.3 Hz*)	7.32 (2H, d, *J=16.2 Hz*)	-
$H_{\omega2}$	7.57 (2H, d, *J=16.4 Hz)*	7.57 (2H, d, *J=16.4 Hz)*	7.07 (2H, d, *J=16.5 Hz*)	-
$H_{\alpha*}$	8.53 (2H, d, *J=6.1 Hz*)	-	-	-
$H_{\beta*}$	7.51 (2H, d, *J=6.2 Hz)*	-	-	-
Hγ*	7.66 (2H, d, *J=8.7 Hz*)	-	-	-
$H_{\omega1*}$	7.29 (2H, d, *J=15.7 Hz)*	-	-	-
$H_{\omega2*}$	7.53 (2H, d, *J=16.4 Hz)*	-	-	-
	2,2'-Bipyridine			
H_3	8.58 (1H, d, *J=8.1 Hz*)	8.59 (2H, d, *J=8.2 Hz*)	-	8.83
$H_{3'}$	8.55 (1H, d, *J=8.0 Hz*)	8.56 (2H, d, *J=8.0 Hz*)	-	8.83
H_7	8.71 (1H, d, *J=8.2 Hz*)	8.72 (2H, d)	-	8.83
$H_{7'}$	8.62 (1H, d, *J=8.2 Hz)*	8.62 (2H, d, *J=8.1Hz)*	-	8.83
H_4	7.91 (1H, d, *J=8.1 Hz*)	7.92 (2H, d *J=7.8 Hz*)	-	8.23
$H_{4'}$	7.92 (1H, d, *J=8.2 Hz*)	7.94 (2H, d *J=7.5 Hz*)	-	8.23
H_8	8.17 (1H, t, *J=7.6 Hz*)	8.18 (2H, t, *J=7.8 Hz*)	-	8.23
$H_{8'}$	8.17 (1H, t, *J=7.6 Hz*)	8.18 (2H, t, *J=7.8 Hz*)	-	8.23
H_5	7.28 (1H, t, *J=6.9 Hz*)	7.29 (2H, t, *J=6.7 Hz*)	-	7.59

$H_{5'}$	7.38 (1H, t, *J=6.7 Hz*)	7.38 (2H, t, *J=6.7 Hz*)	-	7.59
H_9	7.72 (1H, t, *J=6.7 Hz*)	7.72 (2H, t, *J=6.6 Hz*)	-	7.59
$H_{9'}$	7.89 (1H, t, *J=6.5 Hz*)	7.89 (2H, t *J=6.6 Hz*)	-	7.59
H_6	7.79 (1H, d, *J=5.7 Hz*)	7.80 (2H, d, *J=5.8 Hz*)	-	8.07
$H_{6'}$	8.10 (1H, d, *J=5.7 Hz*)	8.11 (2H, d, *J=5.8 Hz*)	-	8.07
H_{10}	8.73 (1H, d *J=5.0 Hz*)	8.73 (2H, d)	-	8.07
$H_{10'}$	10.08 (1H, d, *J=5.6 Hz)*	10.08 (2H, d, *J=5.6 Hz)*	-	8.07

[a] Data obtained in our laboratory (10^{-2} mol dm^{-3} in CD_3Cl).

[b] Data from Constable E.C.; Seddon K. R.; *Inorg. Chim. Acta*, **1983,** *70*, 251.

[c] Coupling constants for *trans*- double bonds are approximately 16 Hz.

Table 2: ^{13}C-NMR Chemical shifts (ppm) for the $[Ru(bpy)_2Cl(BPEB)]PF_6$ and $[\{Ru(bpy)_2Cl\}_2(BPEB)](PF_6)_2$ complexes in $(CD_3)_2CO$.

Carbon	δ (ppm)			
	Mononuclear	Binuclear	Free Ligand[(a)]	$[Ru(bpy)_3]^{+2}$ [(b)]
1,4-bis[2-(4-pyridyl)ethenyl]benzene				
C_α	154.16	154.25	150.4	-
C_β	122.75	122.80	121.1	-
C_δ	146.32	146.24	144.7	-
$C_{\omega1}$	127.39	126.19	126.7	-
$C_{\omega2}$	135.46	135.32	132.7	-
C_θ	138.30	137.81	136.8	-
C_γ	128.68	128.76	127.7	-
$C_{\alpha*}$	151.10	-	-	-
$C_{\beta*}$	121.64	-	-	-
$C_{\delta*}$	145.22	-	-	-
$C_{\omega1*}$	125.81	-	-	-

$C_{\omega 2*}$	133.09	-	-	-
$C_{\theta *}$	136.46	-	-	-
$C_{\gamma *}$	128.45	-	-	-
		2,2'-Bipyridine		
C_2	158.90	158.93	-	156.2
$C_{2'}$	160.53	160.53	-	156.2
C_{11}	159.46	159.47	-	156.2
$C_{11'}$	159.20	159.23	-	156.2
C_3	123.77	123.80	-	123.5
$C_{3'}$	124.66	124.69	-	123.5
C_7	124.28	124.32	-	123.5
$C_{7'}$	124.10	124.14	-	123.5
C_4	136.84	136.88	-	136.7
$C_{4'}$	137.00	136.33	-	136.7
C_8	137.23	137.04	-	136.7
$C_{8'}$	137.30	137.35	-	136.7
C_5	126.78	126.82	-	121.0
$C_{5'}$	127.96	128.01	-	121.0
C_9	127.75	127.78	-	121.0
$C_{9'}$	127.73	127.42	-	121.0
C_6	152.85	152.88	-	149.1
$C_{6'}$	153.79	153.93	-	149.1
C_{10}	153.05	153.06	-	149.1
$C_{10'}$	153.92	153.82	-	149.1

[a] Data obtained in our laboratory (in CD_3Cl)

[b] Data from Constable E. C., Seddon K. R., *Inorg. Chim. Acta,* **1983**, *70*, 251.