Supplementary Table S1. Dependence of the Line Width of Proton Signals of $[Cu(pdt)_2]^+$ on the Concentration of $[Cu(pdt)_2^{2+}]$ in Acetonitrile-d_3

T/K	$\nu_{Cu(I)}$ /Hz	$\nu_{\sigma\alpha\mu\pi\lambda\varepsilon}$ /Hz	$\pi\Delta\nu/s^{-1}$	k_{ex}/kg mol^{-1}s^{-1}
297.8	25.6	33.5	24.8	99200
282.9	22.1	25.7	11.3	45200
272.9	20.7	22.9	6.91	27600
263.0	19.7	20.3	1.88	7540

Errors of k_{ex} were typically ± 5%.

$[Cu(pdt)_2^+]$ = 9.10 mmol/kg. $[Cu(pdt)_2^{2+}]$ = 0.25 mmol/kg.

Sapplementary Table S2. Dependence of the Line Width of Proton Signals of $[Cu(pdt)_2]^+$ on Temperature in acetonitrile-d_3

T / K	k / s^{-1}
297.8	51 ± 5
282.9	42 ± 4
272.9	35 ± 3
263.0	33 ± 3

$[Cu(pdt)_2^+]$ = 9.10 mmol/kg.

Supplementary Table S3. Observed rate constants for the reduction reaction of $[Cu(pdt)_2]^{2+}$ by decamethylferrocene in acetonitrile

T / K	10^4 [decamethylferrocene] / mol kg^{-1}	k_{obs} / s^{-1}
278.2	0.164	3.98±0.21
	0.168	6.24±0.31
	0.224	7.48±0.22
	0.260	8.37±0.44
	0.292	11.1±0.5
	0.446	14.9±0.4
	0.479	18.7±0.7

	0.481	18.5±0.5
	0.657	27.3±0.9
	0.708	27.3±0.7
	0.989	34.0±0.3
	1.03	35.7±0.6
	1.05	36.7±0.6
	1.06	35.7±1.2
	1.12	38.5±0.8
	1.45	46.2±1.1
	1.51	54.1±0.7
	1.89	62.7±1.0
	2.03	69.6±1.1
	2.41	85.1±1.8
	2.88	100±2
	2.97	96.2±1.8
	3.38	123±2
	4.11	139±2
283.2	0.164	7.60±0.25
	0.168	9.61±0.31
	0.224	10.0±0.4
	0.252	11.1±1.6
	0.260	11.8±0.4
	0.292	14.9±0.3
	0.444	22.0±0.8
	0.446	22.0±0.5
	0.479	23.1±0.5
	0.657	34.9±0.8
	0.696	35.3±1.4
	0.708	36.8±0.8
	0.928	45.6±2.7
	0.989	46.7±1.2
	1.03	48.4±0.7

	1.05	47.1±0.7
	1.12	52.5±0.7
	1.45	65.1±1.4
	1.51	66.7±0.7
	1.89	86.8±1.4
	2.03	89.0±1.9
	2.41	109±2
	2.88	128±2
	2.97	131±3
288.2	0.164	10.3±0.6
	0.168	11.9±0.4
	0.224	13.3±0.5
	0.252	16.9±1.4
	0.260	18.7±0.5
	0.292	21.7±0.7
	0.444	27.7±1.6
	0.446	28.2±0.7
	0.479	33.2±0.5
	0.481	34.0±1.1
	0.657	45.1±0.4
	0.696	44.1±2.6
	0.708	46.8±0.5
	0.928	60.6±1.5
	0.989	58.3±0.8
	1.03	58.4±1.0
	1.05	64.6±1.4
	1.06	65.7±0.6
	1.12	70.1±0.7
	1.45	84.6±0.6
	1.51	86.8±2.3
	1.89	111±1
	2.03	119±2

	2.41	138±1
	2.88	163±2
	2.97	174±2
	3.38	187±2

$[Cu(pdt)_2^{2+}] = 1 \times 10^{-5}$ mol kg^{-1}, I = 0.3 mol kg^{-1} ($TBABF_4$), λ = 350 nm.

Supplementary TableS4. Observed rate constants for oxidation reaction of $[Cu(pdt)_2]^+$ by $[Co(bpy)_3]^{3+}$ in acetonitrile

T / K	$10^3[Co(bpy)_3^{3+}]$ / mol kg^{-1}	k_{obs} / s^{-1}
288.2	0.613	0.850
	0.770	0.872
	1.38	1.36
	1.40	1.38
	1.48	1.35
	1.61	1.57
	1.90	1.63
	2.25	1.79
	2.72	1.82
	2.82	1.87
	3.09	2.10
293.2	0.504	0.935
	0.740	1.14
	0.941	1.26
	1.54	1.69
	1.84	2.08
	2.16	2.12
	2.41	2.27
	2.82	2.51
	2.90	2.58
	0.463	1.10

	0.803	1.35
	1.66	2.19
298.2	1.84	2.71
	2.19	2.66
	2.57	3.04
	3.43	3.53

$[Cu(pdt)_2^{2+}] = 1 \times 10^{-4}$ mol kg^{-1}, $I = 0.1$ mol kg^{-1} ($TBAPF_6$), $\lambda = 500$nm.