Supporting information

Photochemistry and Electron Transfer Kinetics in a Photocatalyst Model Assessed by Marcus Theory and Quantum Dynamics

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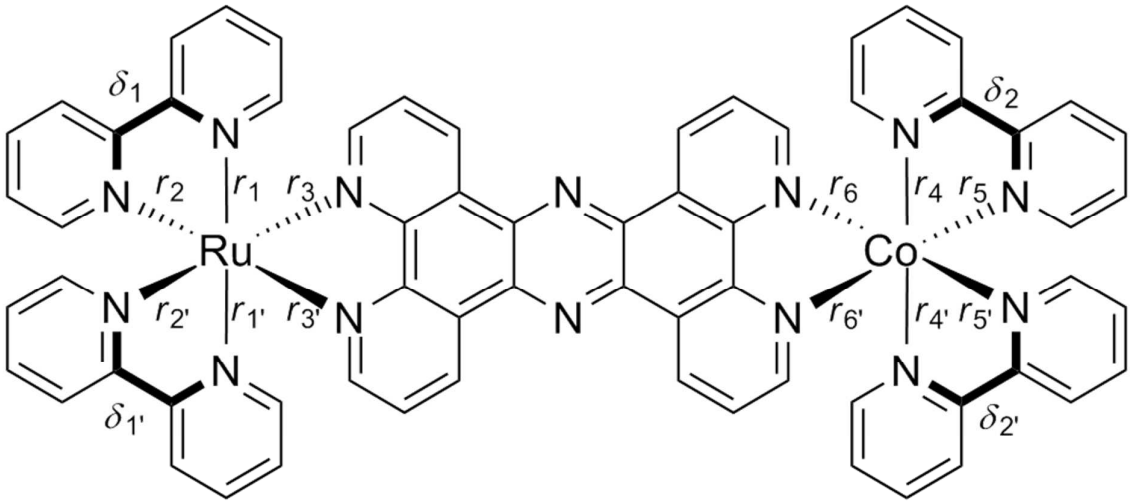
Table S1: Ruthenium-Nitrogen (r_1, $r_{1'}$, r_2, $r_{2'}$, r_3 and $r_{3'}$) and Cobalt-Nitrogen (r_4, $r_{4'}$, r_5, $r_{5'}$, r_6 and $r_{6'}$) as well as bipyridine twisting angles (δ_1, $\delta_{1'}$, δ_2 and $\delta_{2'}$).



	S_0	S_2	T(BL1)	T(BL2)	T(CS1)	T(CS2)	T(CS3)	T(CS5)	T(CR1)	T(CR2)
r_1 / Å	2.101	2.091	2.098	2.093	2.103	2.103	2.093	2.092	2.193	2.734
$r_{1'}$ / Å	2.101	2.091	2.099	2.092	2.104	2.103	2.092	2.092	2.103	2.578
r_2 / Å	2.096	2.118	2.100	2.119	2.093	2.093	2.118	2.118	2.625	2.163
$r_{2'}$ / Å	2.096	2.118	2.102	2.119	2.093	2.093	2.117	2.117	2.104	2.187
r_3 / Å	2.107	2.109	2.102	2.102	2.119	2.119	2.110	2.111	2.189	2.110
$r_{3'}$ / Å	2.108	2.112	2.105	2.105	2.120	2.120	2.112	2.113	2.700	2.128
δ_1 / °	-2	-3	0	-3	0	0	-3	-3	7	-23
$\delta_{1'}$ / °	-2	-3	0	-3	0	0	-3	-3	2	10
r_4 / Å	1.968	1.966	1.966	1.966	1.991	2.227	1.992	2.227	1.971	1.965
$r_{4'}$ / Å	1.969	1.967	1.967	1.967	2.001	2.228	2.000	2.228	1.969	1.967
r_5 / Å	1.962	1.966	1.966	1.966	1.989	1.997	1.989	1.997	1.962	1.962
$r_{5'}$ / Å	1.963	1.967	1.966	1.967	2.215	1.998	2.214	1.997	1.962	1.961
r_6 / Å	1.980	1.973	1.973	1.973	2.265	2.006	2.266	2.007	1.981	1.981
$r_{6'}$ / Å	1.980	1.973	1.974	1.973	2.019	2.006	2.019	2.006	1.981	1.981
δ_2 / °	3	3	3	3	0	10	0	10	3	4
$\delta_{2'}$ / °	3	3	3	3	10	10	11	10	3	4

Table S2: Calculated excited state energies for each state *i* (see Figure 3) along the linear interpolated ET coordinate R_{ET} were fitted the quadratic polynomial, $E(R_{ET}) = a \cdot \left(R - R_{0,a}\right)^2 + b \cdot \left(R - R_{0,b}\right) + c$, respectively, where E_i is the energy, b_i the optimized equilibrium structure and c_i the energy within the equilibrium. All parameters a_i, b_i and c_i are given for each pair of ET states, while additionally the reduced χ^2 values (χ^2_{red}) are provided for a_i to validate the goodness of the fit. As can be easily seen from χ^2_{red} as well as in Figure 3e) and f) no strict quadratic dependency is obtained for the charge-recombination processes along the linear coordinate R_{ET}. The transformation from the LICC coordinate to the coordinates used in the QD simulations, r_6 and $r_{4+r4'}$, are for T(BL1)-T(CS1): $r_6 = 0.029157 \cdot R_{ET} + 1.97354$; for T(BL2)-T(CS3): $r_6 = 0.029289 \cdot R_{ET} + 1.97320$; for T(BL1)-T(CS3): $r_4 + r_{4'} = 0.051653 \cdot R_{ET} + 3.93184$; for T(BL2)-T(CS4): $r_4 + r_{4'} = 0.051744 \cdot R_{ET} + 3.93183$.

donor - acceptor	a_D / eV/(arb.u.)^2	b_D / arb.u.	c_D / eV	R_{0a} / arb.u.	R_{0b} / arb.u.	χ^2_{red} / eV	a_A / eV/(arb.u.)^2	b_A / arb.u.	c_A / eV	R_{0a} / arb.u.	R_{0b} / arb.u.	χ^2_{red} / eV
T(BL1) - T(CS1)	0.00913558	0.00231584	2.0215	0.0000	-8.08712	0.00000015217	0.00803238	-0.0000440499	1.6957	10.0000	-785.872	0.00000022119
T(BL1) - T(CS2)	0.00864085	0.00319325	2.0215	0.0000	-5.46053	0.00000119146	0.00764097	-0.000472578	1.7272	10.0000	-37.5246	-0.00000002391
T(BL2) - T(CS3)	0.00789733	0.0134688	2.1577	0.0000	1.25667	0.00000096679	0.00747769	-0.000496778	1.8511	10.0000	-40.3692	-0.00000002856
T(BL2) - T(CS5)	0.00794113	0.0112796	2.1577	0.0000	1.24653	0.000000007420	0.00732968	-0.000453918	1.8835	10.0000	-49.3562	0.00000144614
T(BL1) - T(CR1)	0.0222923	0	2.0215	0.0000	0	0.0713446	0.0164282	0	1.5571	10.0000	0	0.0541172
T(BL1) - T(CR2)	0.0282096	0	2.0215	0.0000	0	0.193103	0.0210105	0	1.6400	10.0000	0	0.25924

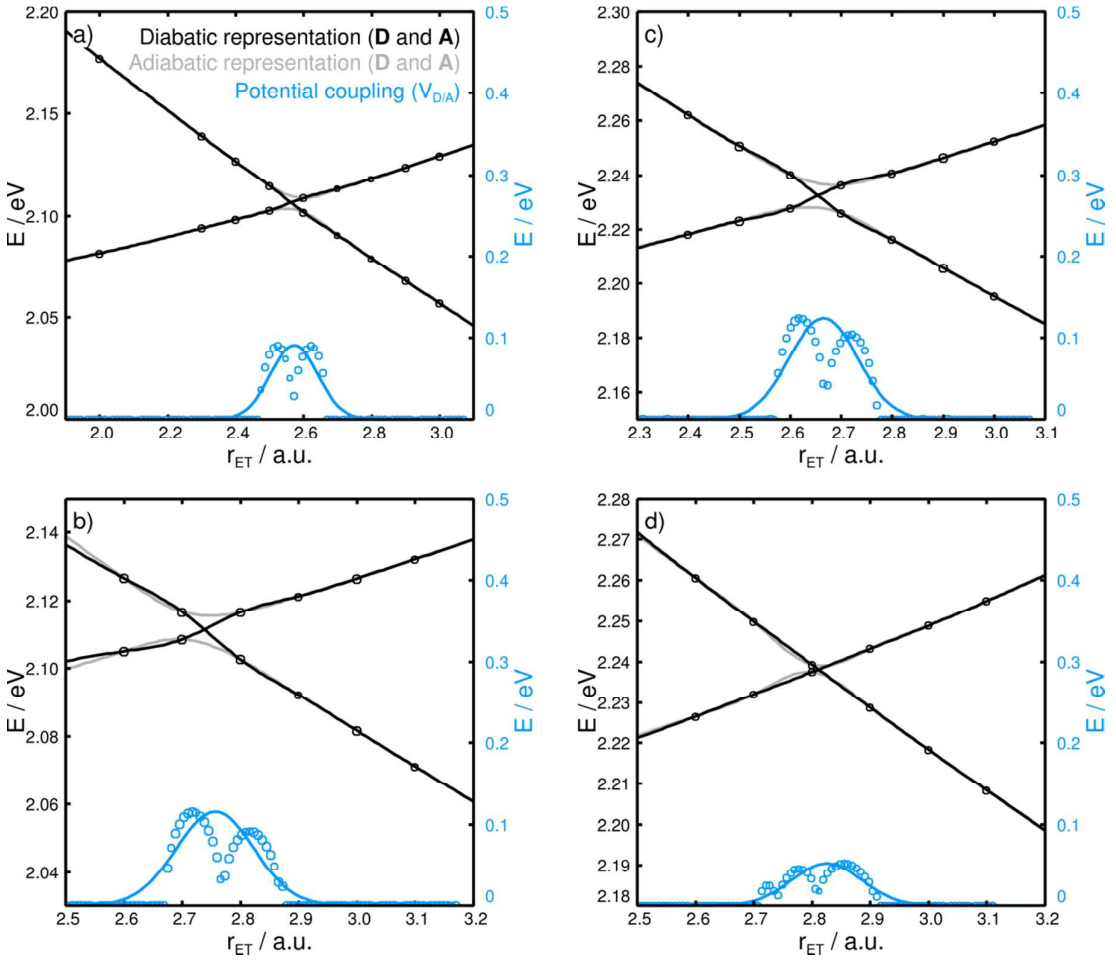


Figure S1: Diabatic (black) and adiabatic (grey) PESs, obtained at the TDDFT level of theory (black circles), and potential coupling matrix elements ($V_{D/A}$, blue) along a LICC (R_{ET}) for a) T(BL1)-T(CS1), b) T(BL1)-T(CS2), c) T(BL2)-T(CS3) and d) T(BL2)-T(CS5).

Table S3: MOs involved in the leading transitions of the bright singlet excited states, the low-lying triplets of ^{3}MLCT character to the bridging ligand T(BL), charge-separated states T(CS) and charge-recombined states T(CR) in the Franck-Condon region.

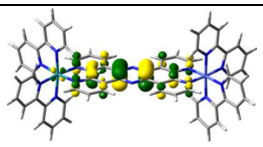
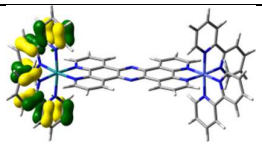
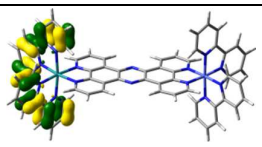
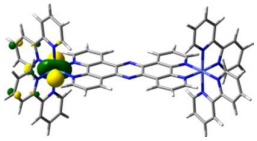
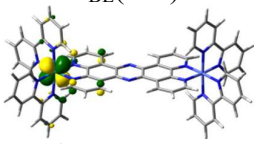
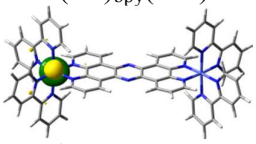
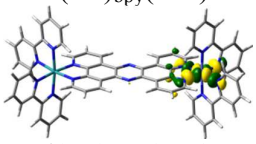
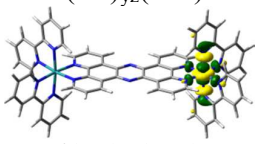
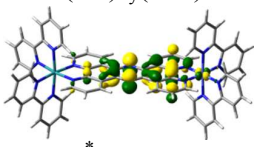
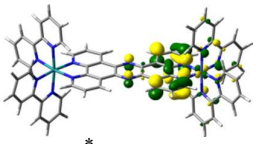
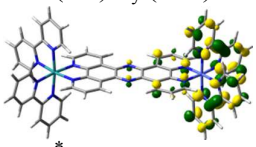
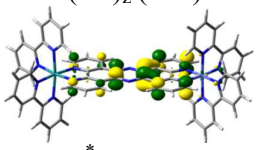
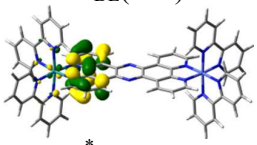
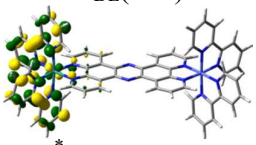
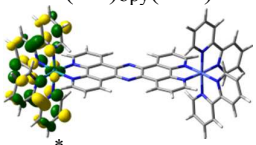
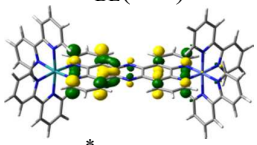
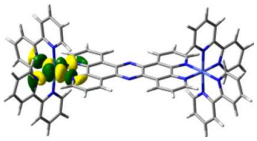
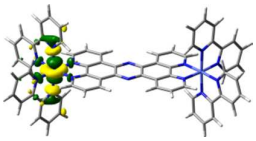
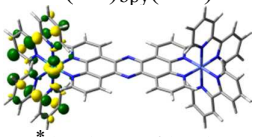
 π_{BL}(271)	 π(Ru)$_{bpy}$(273)	 π(Ru)$_{bpy}$(274)	 d(Ru)$_{yz}$(275)
 d(Ru)$_{xy}$(276)	 d(Ru)$_{xz}$(277)	 d(Co)$_{x^2-y^2}$(278)	 d(Co)$_{z^2}$(279)
 π^*_{BL}(280)	 π^*_{BL}(281)	 π^*(Co)$_{bpy}$(283)	 π^*_{BL}(284)
 π^*_{BL}(285)	 π^*(Ru)$_{bpy}$(286)	 π^*(Ru)$_{bpy}$(287)	 π^*_{BL}(289)
 d(Ru)$_{x^2-y^2}$(304)	 d(Ru)$_{z^2}$(305)	 π^*(Ru)$_{bpy}$+d(Ru)$_{z^2}$ (306)	

Table S4*:* Relative energies of the three singlet states (S_0, S_2 and S_{27}) and 15 triplet states (BL: T(BL1-3), CS: T(CS1-6) and CR: T(CR1-6)), with respect to the S_0 energy in its optimized geometry, involved in the stepwise PET from the Ruthenium to the Cobalt in **RuCo**.

	E^e / eV																	
Equilibrium structure	S_0	S_2	S_{27}	T(BL1)	T(BL2)	T(BL3)	T(CS1)	T(CS2)	T(CS3)	T(CS4)	T(CS5)	T(CS6)	T(CR1)	T(CR2)	T(CR3)	T(CR4)	T(CR5)	T(CR6)
S_0	0.00	2.35	2.88	2.16	2.29	2.35	2.38	2.41	2.54	2.56	2.56	2.58	3.17	3.19	3.41	3.53	3.53	3.60
S_2	0.15	2.21	2.52	2.15	2.16	2.33	2.58	2.60	2.59	2.72	2.62	2.74	3.25	3.39	3.47	3.59	3.55	3.70
T(BL1)	0.14	-	-	2.02	2.26	2.33	2.45	2.47	2.70	2.73	2.73	2.75	3.28	3.31	3.60	3.71	3.71	3.79
T(BL2)	0.14	-	-	2.16	2.16	2.32	2.57	2.60	2.46	2.71	2.49	2.74	3.28	3.39	3.49	3.60	3.57	3.70
T(CS1)	0.77	-	-	2.87	3.10	3.17	1.70	2.62	2.88	2.90	1.96	1.98	3.87	3.91	4.19	4.30	4.29	4.38
T(CS2)	0.75	-	-	2.84	3.07	3.14	2.58	1.73	2.85	2.87	1.99	2.01	3.85	3.89	4.17	4.29	4.27	4.36
T(CS3)	0.79	-	-	3.01	3.00	3.16	2.77	1.84	1.85	2.91	2.78	1.98	3.89	3.97	4.10	4.22	4.18	4.33
T(CS5)	0.77	-	-	2.98	2.97	3.14	2.73	1.87	2.74	2.88	1.88	2.01	3.87	4.01	4.09	4.20	4.16	4.32
T(CR1)	1.96	-	-	4.20	4.53	4.65	4.37	4.39	4.71	4.80	4.74	4.82	1.56	4.64	5.17	2.61	4.98	2.49
T(CR2)	2.04	-	-	4.29	4.57	4.66	4.54	4.51	4.81	4.89	4.85	4.93	4.74	1.64	5.24	2.66	5.05	2.55

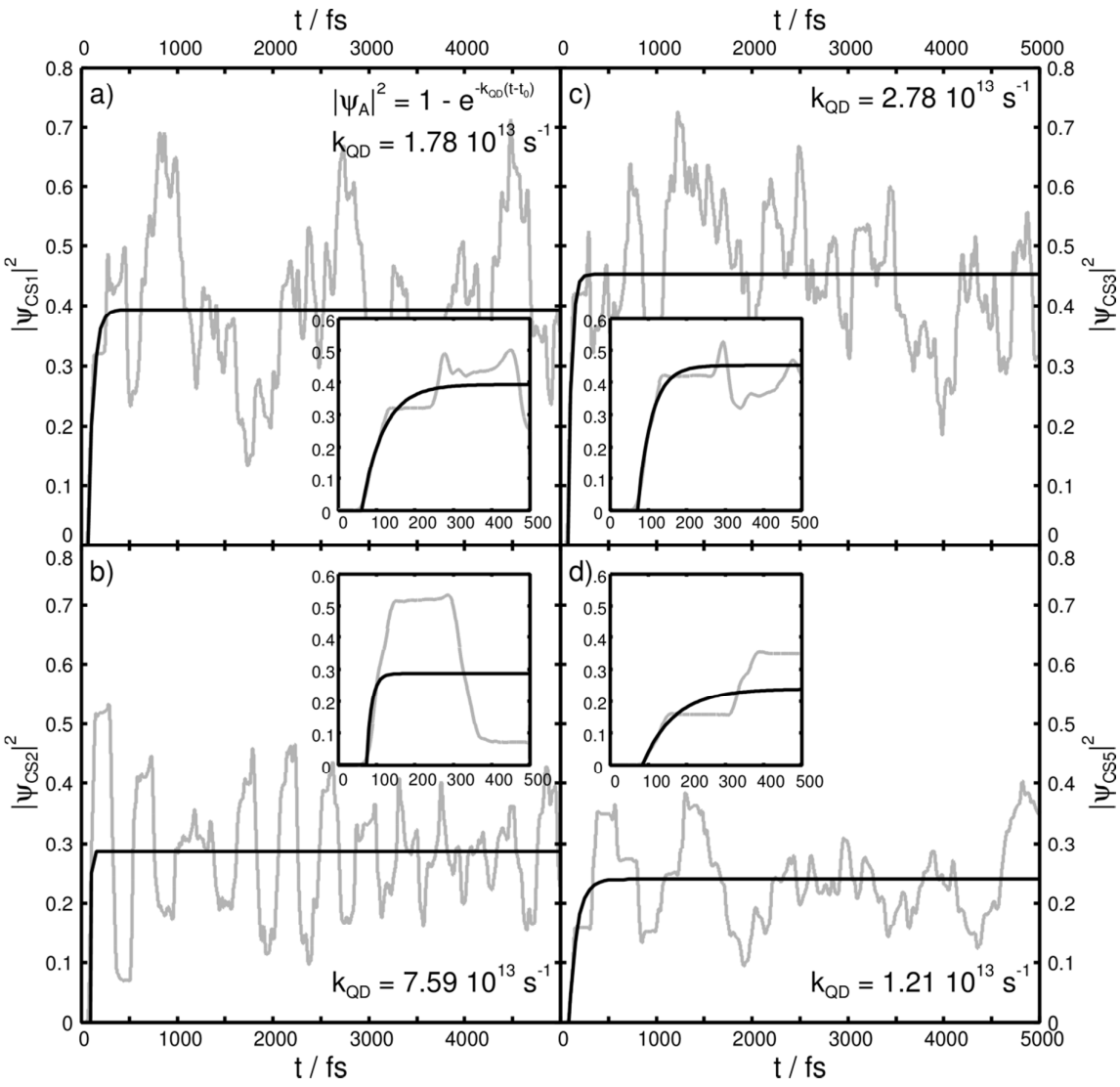


Figure S2: Population of acceptor (CS) state ($|\psi_A|^2$ in grey) and rate constant k_{QD} obtained according to Eq. 6 for the pairs of states: a) T(BL1)-T(CS1), b) T(BL1)-T(CS2), c) T(BL2)-T(CS3) and d) T(BL2)-T(CS5). k_{QD} was fitted for 70 fs $\leq t \leq$ 5000 fs.