**Figure S##. CS decay profiles predicted based on the Monte Carlo simulation technique.** The simulation program has been coded in Pascal using Delphi ver. 5.0 and is available for any purposes at the authors’ website: http:// ##################################/cs\_lifetime\_vs\_migration.zip. This program supposes that several equivalent branches involving a few equivalent viologen acceptor sites are tethered to a single Ru(bpy)32+-type photosensitizer, as depicted below:

This test case supposes that one branch has interaction with two equivalent branches. Even after conducting an inter-branch ET event, an exactly same situation is supposed to be recovered. Therefore, three branches, in this case, should be positioned in a trigonal fashion. Our model also supposes that locations of two MV2+/MV+ sites within a branch are rapidly exchanged or moving around so that inter-branch ET toward every adjacent branch can take place with an equal probability. Under such conditions, ET events can be classified into three types, intra-branch ET, inter-branch ET, and BET, as illustrated in the above picture. Our model supposes that probabilities of conducting these three ET events are different. Here the frequency factors for intra-branch ET, inter-branch ET, and BET are defined by (n\_intra) x (intra\_ff), (n\_inter) x (inter\_ff), and 1, respectively, where n\_intra defines the number of adjacent viologen units within the branch which has already accepted one electron from the photoexcited pigment, and n\_inter is the number of equivalent adjacent branches available for ET, while intra\_ff and inter\_ff are used to further tune the probabilities of intra-branch and inter-branch ET processes, respectively. Note that the frequency factor of BET is not defined as a variable parameter and is fixed as unity in this model. In the model depicted above, n\_intra and n\_inter must be specified as 1 and 2, respectively. In the experiments in Figure S##, intra\_ff = 4 and inter\_ff = 10 are adopted as roughly optimized values to reproduce the experimentally observed CS decay profiles. When the CS decay profile of [Ru(**x,x’-MV4**)3]26+ is examined, an appropriate model can be defined by supposing n\_intra = 1, n\_inter = 4, intra\_ff = 4, and inter\_ff = 10, by which the probabilities of conducting intra-branch ET, inter-branch ET, and BET are given as (n\_intra x intra\_ff)/{(n\_intra x intra\_ff) + (n\_inter x inter\_ff) + 1} = 4/45, (n\_inter x inter\_ff)/{(n\_intra x intra\_ff) + (n\_inter x inter\_ff) + 1} =40/45, and 1/45, respectively. In these experiments, three additional parameters are defined. One is a permeation coefficient (BET) when conducting BET and is defined as BET = 1/3. On the other hand, the permeation coefficient (EM) for conducting all the remaining ET events leading to EM is also defined as unity ( = 1 for intra\_branch and inter\_branch ET events). These specify that the probability of having a BET event is (1/45)x(1/3) = 1/135 in each step, while that of having a migration event is 44/45. A set of parameters defined with n\_intra = 1, n\_inter = 0, intra\_ff = 4, and inter\_ff = 10 is appropriate to examine the behavior of [Ru(bpy)2(**5,5’-MV4**)3]10+ since the inter-branch ET among the 5,5’-positioned branches can be ruled out. The last parameter is the time spent to complete each ET step (tdiv). This include the time spent for diffusion, and is postulated as tdiv = 6 ns in these test cases. In summary, by using the values listed below, the lifetimes of a hundred thousand of CS states were generated by the Monte Carlo technique. As a result, the computed results somehow reflect the observed tendency, which strengthens the validity of such statistical approach in predicting electron migration within a multi-acceptor system.



**Parameters employed in the calculations**:

n\_intra = 1 no. of other MV2+ units within the branch accepted one electron

n\_inter = 0, 1, 2, 3, 4 no. of adjacent branches available for ET

intra\_ff = 4\*\*\* frequency factor to conduct intra-branch ET

inter\_ff = 10 frequency factor to conduct inter-branch ET

BET = 1/3 permeation coefficient for conducting BET

EM = 1 permeation coefficient for conducting self exchange among MV+ and MV2+

tdiv = 6 ns time spent for completing each step

\*\*\* The lower intra\_ff value relative to inter\_ff may be due to the fact that stronger association of a PF6– anion within each branch makes the intra-branch ET more difficult to proceed in compared with the inter-branch ET process.