Charge Transfer versus Charge Transport in Molecular Systems

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In this interdisciplinary research project, we want to help clarify the differences and similarities between electron transfer (ET) and electron transport (ETp) in molecular junctions.[1]

Photoexcitation of transition metal complexes or organic molecules can be used to trigger charge transfer reactions. In recent work, the Wenger group studied photoinduced hole tunneling over a ~2.3 nm distance in two closely related donor-bridge-acceptor compounds (Figure 1).[2] In both cases the hole donor was a photogenerated Ru(III) complex and the hole acceptor was a phenothiazine (PTZ) unit. The molecular bridge connecting the Ru(III) donor and the PTZ acceptor is of the oligo-*p*-phenylene type, once equipped with methyl-substituents (Figure 1A) and once substituted with methoxyl-groups (Figure 1B). The subtle change in bridge substituent from methyl to methoxyl has a dramatic effect on the kinetics for photoinduced charge transfer (Figure 1A/B): The time constant associated with Ru(III)-to-PTZ hole transfer is 20 μs for the methylated bridges but only 17 ns for their methoxylated counterparts.[3] Complementary investigations suggest that hole transfer occurs by a tunneling mechanism in both compounds, but the height of the tunneling barrier is substantially different. The more electron-rich *p*-dimethoxybenzene is oxidized at much less positive electrochemical potential than *p*-dimethylbenzene (Figure 1C). This leads to a lowering of the barrier associated with Ru(III)-to-PTZ hole transfer in the *p*-dimethoxybenzene bridges and an increase of the tunneling probability. The extent of π-conjugation is similar in both bridges, and there is no evidence for incoherent hopping.
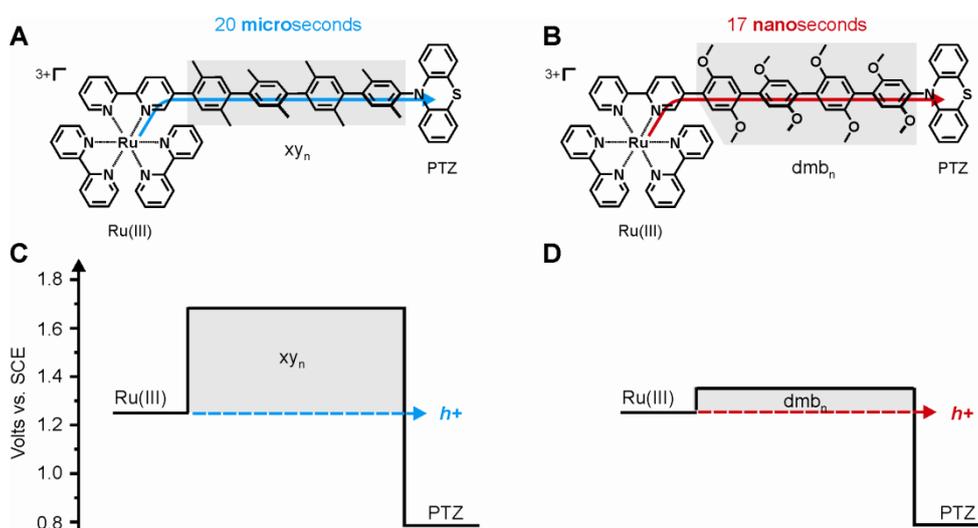
Figure 1. *Photoinduced hole tunneling across structurally similar molecular bridges can occur with drastically different rates due to substantially disparate tunneling barrier heights.[3]*

We would like to explore to what extent charge transfer phenomena similar to that described in the preceding paragraph can be observed for charge transport across single molecules in break junction experiments. In the simplest case, oligo-*p*-dimethylbenzene and oligo-*p*-dimethoxybenzene molecules (Figure 2A) will be equipped with e.g. terminal thiol or pyridine groups for anchoring to gold surfaces, and the distance dependence of single molecule conductance will be determined for molecules that vary in length from ~1.2 to ~4.0 nm. The abovementioned studies indicate that the distance decay constants (β_{HT}) for photoinduced hole tunneling are vastly different for oligo-*p*-dimethylbenzene and oligo-*p*-dimethoxybenzene (β_{HT} = 0.77 Å^{-1} vs <0.2 Å^{-1}).[3]

Whether or not the proposed break junction experiments yield a similarly pronounced difference in the distance dependence of single molecule conductance of bridges I and II (Figure 2A) is an important open question because charge *transfer* in solvated donor-bridge-acceptor compounds and charge *transport* across molecular "wires" are two fundamentally different processes. **The goal of the proposed research is to assess to what extent a molecular bridge which efficiently mediates photoinduced charge transfer in a solvated donor-bridge-acceptor compound will also be an efficient molecular "wire" between two metal electrodes and vice versa.** Particular focus will be on the comparison of the distance dependences of charge transfer (β-values and rate constants) and charge transport (conductance).[4,5]

Our investigations need to be limited to methylated and methoxylated oligo-*p*-phenylenes but may further include even more electron-rich systems such as tetramethoxybenzenes or amino-decorated phenylenes (III, IV, Figure 2B) in which *hole* hopping processes can be anticipated. Alternatively, strongly-electron deficient dimesitylboron-decorated phenylenes (V, Figure 2B) can be used to probe *electron* tunneling or hopping processes. The variable-length bridges from Figure 2A/B will be equipped with terminal thiol or pyridine units for anchoring to gold electrodes for charge transport studies (Figure 2C, top) or with photosensitizer and electron donor units (Figure 2C, bottom) for optical pump-probe investigations of charge transfer in solvated donor-bridge-acceptor compounds.
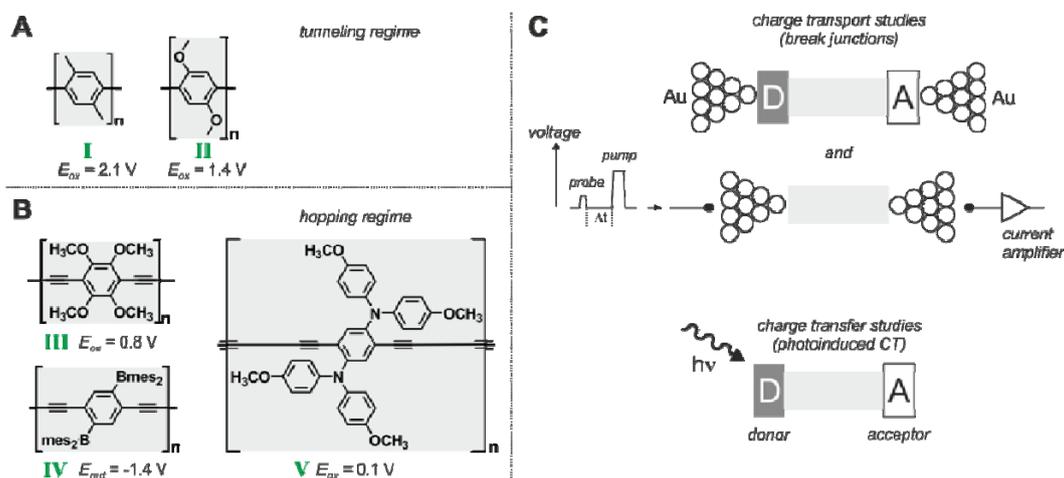
Figure 2. *(A/B) Suitable molecular bridges for comparative studies of (C) charge transport versus charge transfer.*

Synthetic work and optical pump-probe studies of photoinduced charge transfer in solvated donor-bridge-acceptor compounds will be performed in the Wenger group, investigations of time-resolved charge transport will be conducted by the Calame group.

We think that the question to what extent results from photoinduced charge transfer studies in donor-bridge-acceptor compounds can be extrapolated to charge transport processes is of fundamental interest. To date, it was only shown experimentally and theoretically that, depending on the systems and charge transport mechanisms, ET transfer rates and conductance in ETp can be related linearly.[6] Recently however, a power law relation has been observed experimentally.[7] Further clarifying the correlation between ET and ETp at the microscopic scale will require measurements spanning an extended range of time-scales, from seconds down to, potentially, picoseconds. This is the direction we would like to explore, and we are unaware of existing prior studies that took an equally systematic and time-resolved approach as proposed here.

References

1. Nitzan, A.; Ratner, M.A., *Science* **2003**, *300,* 1384*;* Launay, J.-P.*, Coord. Chem. Rev,* **2012**, *257,* 1544.
2. Walther, M. E.; Wenger, O. S., *ChemPhysChem* **2009**, *10*, 1203.
3. Wenger, O. S., *Acc. Chem. Res.* **2011**, *44*, 25.
4. Calame, M., *Chimia* **2010**, *64*, 391.
5. Huber, R.; et al., *J. Am. Chem. Soc.* **2008**, *130*, 1080*.*
6. Adams, DM et al., *J. Phys. Chem.B* **2003**, *107,* 6668; Berlin YA, Ratner, MA, *R. Phys.Chem.* **2005**, *74,* 124; Nitzan, A, *J. Phys. Chem.* **2001**, *105*, 2577.
7. Wierzbinski E; et al., *ACS Nano,* **2013**, *7(6),* 5391.