[3] D. Hoppe, T. Hense, *Angew. Chem.* **1997**, *109*, 2376–2410; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2282–2316.

[4] a) S. T. Kerrick, P. Beak, *J. Am. Chem. Soc.* **1991**, *113*, 9708–9710; b) A. Basu, P. Beak, *J. Am. Chem. Soc.* **1996**, *118*, 1575–1576; c) D. J. Pippel, G. A. Weisenburger, S. R. Wilson, P. Beak, *Angew. Chem.* **1998**, *110*, 2600–2602; *Angew. Chem. Int. Ed.* **1998**, *37*, 2522–2524.

[5] L. Micouin, M. Oestreich, P. Knochel, *Angew. Chem.* **1997**, *109*, 274–276; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 245–246.

[6] C. Darcel, F. Flachsmann, P. Knochel, *Chem. Commun.* **1998**, 205–206.

[7] a) A. Boudier, F. Flachsmann, P. Knochel, *Synlett* **1998**, 1438–1440; b) A. Boudier, P. Knochel, *Tetrahedron Lett.* **1999**, *40*, 687–690.

[8] a) F. Langer, L. Schwink, A. Devasagayaraj, P.-Y. Chavant, P. Knochel, *J. Org. Chem.* **1996**, *61*, 8229–8243; b) L. Micouin, P. Knochel, *Synlett* **1997**, 327–328.

[9] a) D. A. Evans, J. Bartoli, T. Godel, *Tetrahedron Lett.* **1982**, *23*, 4577–4580; b) D. H. Birtwistle, J. M. Brown, M. W. Foxton, *Tetrahedron Lett.* **1986**, *27*, 4367–4370; c) G. Schmid, T. Fukuyama, K. Akasaka, Y. Kishi, *J. Am. Chem. Soc.* **1979**, *101*, 259–260; d) W. C. Still, J. C. Barrish, *J. Am. Chem. Soc.* **1983**, *105*, 2487–2489; e) S. S. Bhagwat, P. R. Hamann, W. C. Still, *Tetrahedron Lett.* **1985**, *26*, 1955–1958.

[10] I. Klement, P. Knochel, *Synlett* **1996**, 1004–1006.

[11] Et_2BH is generated by the reaction of $BH_3 \cdot Me_2S$ (1 equiv) with Et_3B (2 equiv, RT, 4 d); compare with ref. [8].

[12] P. Knochel, M. C. P. Yeh, S. C. Berk, J. Talbert, *J. Org. Chem.* **1988**, *53*, 2390–2392.

[13] M. C. P. Yeh, P. Knochel, *Tetrahedron Lett.* **1989**, *30*, 4799–4802.

[14] For radical C–C bonding reactions via organoboranes, see: C. Ollivier, P. Renaud, *Chem. Eur. J.* **1999**, *5*, 1468–1473.

[15] 2D-COSY and NOESY NMR analysis was used to establish the relative stereochemistry of the hydroboration step for systems **1**, **8**, and **11**–**13**. The monocyclic protected allylic alcohols **1** and **8** had to be converted initially into the corresponding bicyclic acetals (hydroboration, oxidation, *p*-toluenesulfonic acid catalyzed acetalization).

[16] S. A. Bal, A. Marfat, P. Helquist, *J. Org. Chem.* **1982**, *47*, 5045–5050.

[17] T. Hiyama, M. Shinoda, H. Saimoto, H. Nozaki, *Bull. Chem. Soc. Jpn.* **1981**, *54*, 2747–2758.

[18] J.-L. Luche, *J. Am. Chem. Soc.* **1978**, *100*, 2226–2227.

[19] D. Askin, R. P. Volante, R. A. Reamer, K. M. Ryan, I. Shinkai, *Tetrahedron Lett.* **1988**, *29*, 277–280.

Distance-Dependent Electron Transfer in Au/Spacer/Q-CdSe Assemblies

Erik P. A. M. Bakkers, Albert W. Marsman,
Leonardus W. Jenneskens, and
Daniël Vanmaekelbergh*

Long-range electron transfer, that is, over distances of several molecular units, is an important phenomenon in biological systems; its role in protein and DNA function is currently a central issue in biological and chemical research.[1] Long-range electron tunneling also plays a key role in (opto)electronic devices. For instance, further miniaturization of the silicon-based metal/oxide/semiconductor transistor is seriously hindered due to electron tunneling through the oxide layer of molecular thickness.[2] The dependence of electron transfer rate on the tunneling distance is an important topic in chemistry, biology, and physics. The electron transfer rate constant k between a filled (donor) and empty (acceptor) level is given by Equation (1), where H_{DA} describes the electronic coupling between the donor and acceptor, and $F(\Delta G,\lambda)$ is the Franck–Condon factor.[3]

$$k = (2\pi/\hbar)\, H^2_{DA}\, F(\Delta G,\lambda) \qquad (1)$$

To enable elastic tunneling, a nuclear reorganization in the donor–acceptor system is often required: The expression $F(\Delta G,\lambda)$ accounts for the thermal activation that depends on the Gibbs free energy change ΔG and the reorganization energy parameter λ of the system. Due to the separation r between the electron donor and acceptor, the electronic coupling is much weaker than the maximum value $H_{DA,max}$ and decays exponentially with r [(Eq. (2)].

$$H^2_{DA} = H^2_{DA,\,max}\, e^{-\beta r} \qquad (2)$$

Much research has been devoted to the experimental determination of the decay parameter β in crystalline and amorphous solids and in biologically relevant (protein, DNA) systems. Interestingly, the values for β, 0.1–1.5 Å^{-1}, are considerably smaller than the values for tunneling through a vacuum and depend markedly on the nature of the bridging molecule(s) between the donor and acceptor.[1] An inherent problem in a reliable determination of β is the possible dependence of the Franck–Condon factor $F(\Delta G,\lambda)$ on the separation r because of Coulombic interactions in the reactant, product, and transition state.[1, 3] The electron transfer rate is often investigated by time-resolved optical methods, for instance, fluorescence quenching of the photoexcited electron donor or acceptor. For a reliable interpretation of the data, the mechanism of excited-state decay, which involves light emission, electron transfer, and/or electron–phonon coupling, must be known. In addition, this mechanism must not change when the distance between donor and acceptor is increased by using larger bridging molecules.

Herein, we describe a class of assemblies, in which a photoexcitable entity (here a quantum dot, Q, in the form of a nanocrystalline particle) is covalently linked to a metal by spacer molecules of variable length. Relaxation of the excited state in Q may occur by two electronic transfers between the metal and Q; energy relaxation then occurs in the metal phase. Figure 1 shows an excited state in Q. Decay by two consecutive electron transfers may compete with relaxation of the excited state in Q. For this to occur, the Fermi level of the metal must be below the energy level of the excited electron in Q (the LUMO in Figure 1) but above the empty energy level (the unoccupied trap in Figure 1). Electron transfer between the energy levels in Q and the continuum of electron levels in the metal does not involve thermal activation; this means that the rate is solely determined by the electronic coupling between donor and acceptor [see Eq. (1) and (2)].

---

[*] Dr. D. Vanmaekelbergh, Dr. E. P. A. M. Bakkers
Chemistry and Physics of Condensed Matter
Debye Institute, Utrecht University
P.O. Box 80000, 3508 TA Utrecht (The Netherlands)
Fax: (+31) 30-253-2403
E-mail: Daniel@phys.uu.nl

Dr. A. W. Marsman, Prof. Dr. L. W. Jenneskens
Department of Physical Organic Chemistry
Debye Institute, Utrecht University,
P.O. Box 80000, 3508 TA Utrecht (The Netherlands)

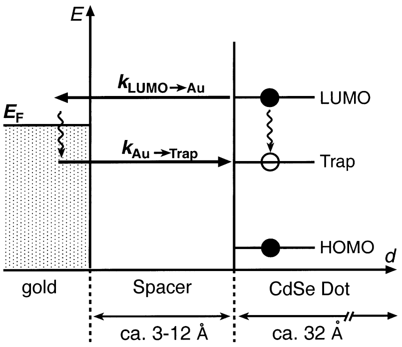
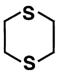


Figure 1. Energy diagram of a photoexcited semiconductive Q particle linked to a metal by a spacer molecule. The relaxation of the photoexcited state by electron transfer between the metal and the Q particle may effectively compete with direct decay (vertical arrow on the right-hand side), if the Fermi level of the metal is located between the energy level occupied by the photoexcited electron (the LUMO) and the unoccupied level (a trapped hole).

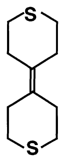
This simplification allows a direct interpretation of experimental data. In addition, if the metal/spacer/Q assembly is used as an electrode, the rates of electron transfer can be measured electrically, namely, by time-resolved measurement of the photoinduced current in the external circuit. Clearly, metal/spacer/Q assemblies are ideal systems for the study of the distance dependence of electron transfer.

We present results obtained with an Au/spacer/Q-CdSe system (Q-CdSe is a size-quantized CdSe paticle) used as a working electrode in a photoelectrochemical cell, which contains also a counter and reference electrode. Three bissulfide spacer molecules (**1**–**3**) have been used; they are rigid insulating species with lengths of 3.4, 7.7, and 11.8 Å, respectively. These molecules form compact self-assembled monolayers (SAM) on gold with a tilt angle of 23° with respect to the normal axis.[4] AOT-stabilized Q-CdSe colloid crystals in heptane (AOT = bis(2-ethylhexyl)sulfosuccinate) were prepared according to a procedure reported in the literature.[5] Figure 2a shows the absorption spectrum of the suspension. The size of the crystals was 32 ± 4 Å, as determined by transmission electron microscopy (TEM) and optical absorbance spectroscopy. The nanocrystals are anchored as a monolayer on the Au/spacer system by immersing this system in the colloidal suspension for several hours. A scanning tuneling microcopy (STM) image of the system is presented in Figure 2b. Evidence for a covalent linking of the nanocrystals to the spacer molecule by S–Cd bonds is provided by the robust mechanical properties of the Au/spacer/Q-CdSe system during repeated atomic force microscopy (AFM) and STM scans and also by the fact that the CdSe dots did not attach to the Au/SAM when the monosulfide spacer molecules **4** and **5**, instead of **1**–**3**, were used. Other evidence for covalent S–Cd bonds is provided in ref. [6].

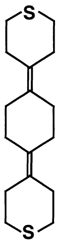
3.4 Å 7.7 Å 11.8 Å



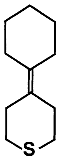
1



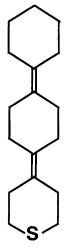
2



3



4



5

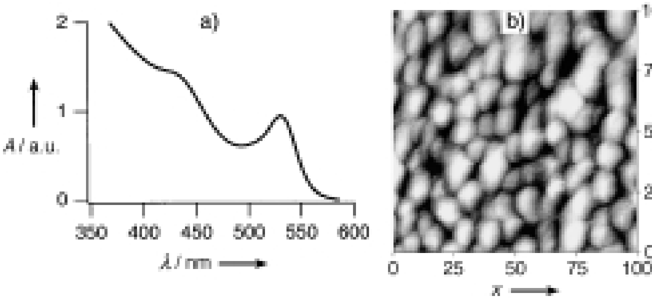


Figure 2. a) Absorption spectrum of a suspension of the size-quantized CdSe colloids (diameter 32 ± 4 Å). b) STM image of the CdSe particles chemisorbed on a gold surface covered with a SAM of **2**.

The Au/spacer/Q-CdSe electrode was illuminated with an argon ion laser ($\lambda = 457$ nm). A harmonic contribution to the intensity, $\tilde{\Phi}(\omega)$, was obtained with an acoustooptic modulator (frequency range $1 < \omega < 10^5\,\text{s}^{-1}$). The harmonically varying current density $\tilde{j}(\omega)$ was measured in the external circuit between the working and counter electrodes. A typical spectrum of the optoelectrical transfer function $\tilde{j}(\omega)/e\tilde{\Phi}(\omega)$ for Au/**2**/Q-CdSe is shown in Figure 3a; similar spectra are obtained with the spacer molecules **1** and **3**. The spectrum can be explained by assuming a long-lived excited state is formed in Q-CdSe upon excitation with light of energy $h\nu > E_{\text{gap}}$. This is confirmed by results from transient luminescence spectroscopy.[7] At sufficiently high frequencies, $\tilde{j}(\omega)/e\tilde{\Phi}(\omega)$ is zero. An "anodic" vector develops with decreasing frequencies, which is indicative of electron transfer from the photoexcited Q-CdSe particles to the gold. The anodic vector reaches a maximum and subsequently diminishes to zero with decreasing frequency; electron transfer from the nanocrystal to gold is gradually compensated by the slower transfer in opposite direction, from the gold to an empty state in Q-CdSe particles. Thus, decay of the excited state by transfer of an electron from Q-CdSe to gold and back to Q-CdSe competes effectively with intraparticle decay (Figure 1). By scanning the Fermi level of the gold electrode, we found that the long-lived state of the Q-CdSe particles consists of an electron in the LUMO, located at around 0.9 eV (versus SCE), and an empty level (trapped hole), 0.5 eV below the LUMO. Thus, photoinduced electron transfer is due to a long-lived state (lifetime ≥ 1 ms, see later) of low energy (0.5 eV). We should remark that this state results from the decay of a primary exciton (electron in the LUMO, hole in the HOMO) in the Q-CdSe particle. From the previous argumentation and from an analytical treatment, it follows that the characteristic frequencies ω_a and ω_b correspond to the rate constants $k_{\text{LUMO}\rightarrow\text{Au}}$ and $k_{\text{Au}\rightarrow\text{Trap}}$, respectively.[8] These rate constants are independent of temperature over the range 293–333 K, which shows that electron transfer is not thermally activated. In addition, the rate constants were (nearly) independent of the Fermi level in

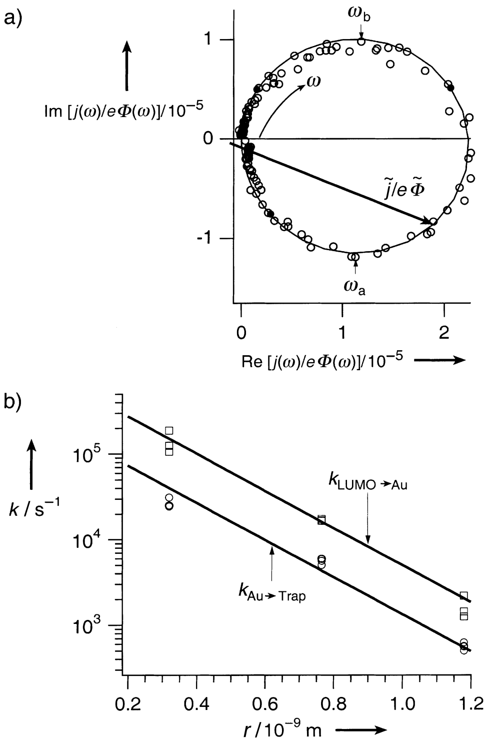


Figure 3. a) Plot of the transfer function $\tilde{j}(\omega)/e\tilde{\Phi}(\omega)$ in the complex plane obtained with a Au/**2**/Q-CdSe electrode in a photoelectrochemical cell (Pt counter electrode, SCE reference electrode, aqueous 1M KCl solution). The spectrum is quantitatively explained by two photoinduced electron transfer steps between Q-CdSe and gold; the characteristic frequencies ω_a and ω_b correspond to the rate constants $k_{\mathrm{LUMO}\rightarrow\mathrm{Au}}$ and $k_{\mathrm{Au}\rightarrow\mathrm{Trap}}$, respectively.[8] b) Semilogarithmic plot of the rate constants $k_{\mathrm{LUMO}\rightarrow\mathrm{Au}}$ and $k_{\mathrm{Au}\rightarrow\mathrm{Trap}}$ versus the length r of the spacer molecules **1**–**3**; the results shown were obtained for three samples for each spacer.

the gold electrode between 0.5 and 0.9 eV (versus SCE). Both observations show that the Franck–Condon factor $F(\Delta G,\lambda)$ is a constant and, hence, that changes in the rates of electron transfer are directly related to the electronic coupling. It was also found that the optoelectrical transfer function is independent of the background light intensity, to indicate that effects due to two-photon absorption in the Q-CdSe particles are unimportant.

The dependence of $k_{\mathrm{LUMO}\rightarrow\mathrm{Au}}$ and $k_{\mathrm{Au}\rightarrow\mathrm{Trap}}$ on the length of the rigid spacer molecule was investigated by measurement of the $\tilde{j}(\omega)/e\tilde{\Phi}(\omega)$ spectrum for each Au/spacer/Q-CdSe system for spacer molecules **1**–**3**. The results are presented in Figure 3b. Both $k_{\mathrm{LUMO}\rightarrow\mathrm{Au}}$ and $k_{\mathrm{Au}\rightarrow\mathrm{Trap}}$ decrease exponentially with increasing distance ($k = k_{\mathrm{max}}\mathrm{e}^{-\beta r}$), the parameter β is 0.50 ± 0.05 Å^{-1}. This β value is about one half of that found for most proteins and comparable to values for DNA strands.[1, 3] Using the Gamow formula for tunneling through vacuum, $\beta = 2\sqrt{2m_eV/\hbar^2}$, we estimate a β value of 2.2 Å^{-1} assuming an energy barrier V of 4 eV. The much weaker attenuation of the electron transfer rates with distance in the Au/spacer/Q-CdSe system is indicative of strong coupling between Au and CdSe over the disulfide spacer molecules. It shows that there is a strong orbital overlap between Au and S on one side and between Cd and S on the other side of the spacer molecule. In addition, there must be a strong through-bond interaction in the spacer molecules. Photoelectron spectroscopy (He I) of the spacer molecules proves that there is a strong interaction between the two $3p_\pi$ lone pair (Lp) orbitals of the terminating sulfur atoms ($\mathrm{Lp}_\pi(\mathrm{S})$) through the olefinic π bond orbitals and the $\mathrm{H_{ax}}$-C-C-$\mathrm{H_{ax}}$ σ orbital system of the cyclohexyl rings; the orbital-energy differences $\Delta\mathrm{Lp}_\pi(\mathrm{S})$ are for **1**–**3** 0.45, 0.4, and 0.3 eV, respectively.[4] This is in agreement with the weak distance dependence of the rate of electron transfer in the Au/spacer/Q-CdSe assemblies reported here.

In summary, for covalently bound metal/spacer/Q assemblies, in which Q is a light-absorbing nanocrystal, photoinduced electron transfer can occur without thermal activation. This allows an unambiguous determination of the distance dependence of the electron transfer rate using spacer molecules of variable length. This is illustrated with CdSe quantum dots bound to the metal with rigid bisulfide spacer molecules.

Received: January 13, 2000 [Z14532]

---

[1] a) C. C. Moser, J. M. Keske, K. Warncke, R. S. Farid, P. L. Dutton, *Nature* **1992**, *355*, 796–802; b) G. L. Closs, J. R. Miller, *Science* **1988**, *240*, 440–446; P. F. Barbara, T. J. Meyer, M. A. Ratner, *J. Phys. Chem.* **1996**, *100*, 13148–13168; d) S. O. Kelley, J. K. Barton, *Science* **1999**, *283*, 375–381.

[2] P. A. Packan, *Science* **1999**, *285*, 2079–2080, and references therein.

[3] R. A. Marcus, N. Sutin, *Biochim. Biophys. Acta* **1985**, *811*, 265–322.

[4] a) A. W. Marsman, PhD thesis, University of Utrecht (The Netherlands) **1999**, Chap. 6; b) The He I photoelectron spectra of the spacer molecules **1**–**3** were measured at the University of Heidelberg by Prof. Dr. R. Gleiter and co-workers, A. W. Marsmann, R. W. A. Havenith, S. Bethke, L. W. Jenneskens, R. Gleiter, J. H. van Lenthe, M. Lutz, A. L. Spek, *J. Org. Chem.* **2000**, in press. c) For photoinduced intramolecular electron transfer in donor–acceptor-substituted analogues of **1**–**3**, see: F. J. Hoogesteger, C. A. van Walree, L. W. Jenneskens, M. R. Roest, J. W. Verhoeven, W. Schuddeboom, J. J. Piet, J. M. Warman, *Chem. Eur. J.* **2000**, in press.

[5] M. L. Steigerwald, A. P. Alivisatos, J. M. Gibson, T. D. Harris, R. Kortan, A. J. Muller, A. M. Thayer, T. M. Duncan, D. C. Douglas, L. E. Brus, *J. Am. Chem. Soc.* **1988**, *110*, 3046–3050.

[6] V. L. Colvin, A. N. Goldstein, A. P. Alivisatos, *J. Am. Chem. Soc.* **1992**, *114*, 5221. The capping of the Q particles is the same as used in our work; the SAM layer consisted of hexanedithiol.

[7] M. G. Bawendi, P. J. Carroll, W. L. Wilson, L. E. Brus, *J. Chem. Phys.* **1992**, *96*, 946–954.

[8] E. P. A. M. Bakkers, E. Reitsma, J. J. Kelly, D. Vanmaekelbergh, *J. Phys. Chem. B.* **1999**, *103*, 2871–2788.